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Assessment of Welfare Effects and the Secondary Air Quality Standard for Ozone

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Strategies and Air Standards Division
Office of Air Quality Planning and Standards
U. S. Environmental Protection Agency
Research Triangle Park, NC

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Review of the effects of ozone upon vegetation and materials in an attempt to justify the establishment of national secondary ambient air quality standards for ozone. The report concludes that ozone standards should be set on the basis of its effects on vegetation, particularly economically important crops, where effects are well documented rather than upon its potential for causing materials damage. Provides analyses of alternative sets of ozone standards. Recommended standard proposed is .08 ppm.

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I. Summary

The Clean Air Act mandates the setting of a national secondary ambient air quality standard to protect the public welfare from any known or anticipated adverse effects associated with the presence of an air pollutant in the ambient air. Ozone and other photochemical oxidants constitute a form of air pollution that affects vegetation and materials. The resultant economic loss has been estimated to be in the range of several hundred million dollars per year nationwide. Nonquantifiable losses to the natural environment occur as well.

Exposure of vegetation to harmful levels of ozone may result in leaf injury, decreased growth and yield, or reproductive effects. Visible leaf injury is the most readily detectable symptom of ozone exposure and for this reason has commonly been used in attempts to quantify damage to economic crops. Decreases in growth and yield can occur without such visible symptoms; however, since leaf injury is the most readily detectable and frequently reported symptom of ozone damage, this effect provides the best available data base for evaluating alternative standard levels. While it is not currently possible to make definite correlations of foliar injury with reductions in yield, several investigators have suggested that foliar injury rates in the range of 5 to 10 percent could produce detectable reductions in growth or yield, depending on the timing of the injury and other environmental factors. Ozone exposures which may be reasonably expected to produce injury ratings within this range in commercially important crops or important indigenous flora are undesirable; therefore, the basis of the secondary National Ambient Air Quality Standard (NAAQS) for ozone will be to protect against such exposures.

The effects of ozone on vegetation are not linearly dependent on the dose (product of concentration and exposure duration) sustained by the plant. A given dose applied over a short period of time is more damaging than if it were applied over a longer period. A mathematical model has been used to summarize for several crops the experimental results which depict the variation in foliar response with short-term (0.5-hour to 8-hour) ozone exposures. Based on these results, no commercially important crop is predicted to receive more than 3 percent leaf injury as a result of short-term peak ozone exposures at sites where an hourly average concentration above 0.08 ppm is expected to occur only once per year. Such a level of air quality should thus protect agricultural crops from detectable effects on growth and yield due to short-term peak ozone exposures, even after allowing for possible interaction between ozone and other air pollutants. In addition, studies which have examined the effects of long-term, intermittent ozone exposures on growth and yield of vegetation indicate that no detectable effects should occur as a result of the long-term pattern of ozone exposures anticipated when an hourly average concentration of 0.08 ppm is expected to be exceeded only once per year.

It should be noted that the above predictions were based on air quality relationships (e.g., the ratio of the 1-hour-average peak concentration to the corresponding 8-hour-average value) which were judged to be representative for urbanized areas where an hourly average concentration above 0.08 ppm is expected to occur only once per year. Equivalent relationships for rural areas have not been quantified, yet there is reason to believe that higher 8-hour-average concentrations may occur at a rural site than at an urban site when both are attaining the same hourly average standard. EPA has attempted to factor this uncertainty into its analysis of alternative hourly average standard levels, but is soliciting comments as to whether the standard should be set for an averaging time of 8 hours rather than 1 hour in order to insure the protection of vegetation in rural areas.

Material damage due to ozone can be described as an acceleration of aging processes, e.g., rubber cracking, dye fading, and paint weathering. In contrast to the effects of ozone on vegetation, these effects appear to be governed in a linear fashion by the ozone dose sustained by the material. As a result, the annual average concentration will determine the rate at which material damage occurs, and any nonzero ozone concentration (including natural background levels) will contribute to the deterioration of sensitive materials if the exposure is sustained long enough. In remote areas selected to be as free from man-made influences as possible, annual average ozone concentrations are comparable with those seen in urban areas, due to strong nighttime scavenging of ozone in urban areas by man-made pollutants. For the above reasons, no effect-based rationale can be offered to decide the level of the secondary standard needed to protect materials. As a result, EPA proposes to evaluate the level of the secondary standard principally on the basis of the air quality required to protect vegetation from growth and yield effects, since there is no level at which some material damage will not occur given sufficient time.

Based on the preceding considerations, EPA proposes to set the secondary ozone air quality standard level at an hourly average concentration of 0.08 ppm expected to be exceeded only once per year.

A review of air quality data in remote areas indicates that ozone concentrations may occasionally approach and infrequently even go above the proposed standard level in situations when man-made influences are negligible. These events appear more likely to occur at higher elevations during the winter and spring months. Comparison of this data with urban and non-remote rural ozone data indicates that the bulk of the ozone problem observed during the summer months in the latter areas is due to man-made influences.

II. The Need for a Secondary NAAQS for Ozone

As the major constituent of the air pollutant category termed photochemical oxidants, ozone damages vegetation and materials to an extent that endangers the public welfare. The nationwide economic loss sustained at the farm level due to damage of vegetation by ozone and other photochemical oxidants has been estimated to approach $300 million annually.[1] At least 18 different crops can no longer be grown in the Los Angeles air basin due to air pollution damage,[2] predominantly oxidant damage. Much more difficult to quantify are the losses resulting from oxidant damage to natural ecosystems such as forests. For example, long-term oxidant exposure in the San Bernardino Mountains near Los Angeles has injured conifer forests there, reducing timber production and affecting reproduction of the conifer population, thereby diminishing the economic, recreational, and ecological (life-support) value of this natural resource to the residents of the region.[3]

In addition to its effects on biological systems, ozone accelerates the aging process of materials, with cracking of rubber products being a major example of this effect. A 1970 study estimated nationwide losses at the consumer level due to both air pollution (ozone) damage to rubber products and the costs of preventive measures to be $500 million annually.[4]

The above summary of the detrimental effects of ozone on both economic and aesthetic aspects of public welfare demonstrates the need for a secondary air quality standard to protect the public welfare. The following sections provide detailed discussions of the scientific evidence regarding ozone effects and air quality data, and finally an analysis of alternative standard levels.

III. Effects of Ozone and Other Photochemical Oxidants

A. Vegetation Damage:

1. Monitoring Methods and Data Reliability: Most plant scientists measuring the effects of controlled ozone exposures or ambient oxidant episodes on vegetation have used wet chemical (potassium iodide, or KI) methods for monitoring the pollutant concentrations.[5] When monitoring ambient air, KI methods respond to other oxidants besides ozone (O_3), such as nitrogen dioxide (NO_2) and peroxyacetylnitrate (PAN), and their response is diminished by the presence of reducing compounds such as sulfur dioxide (SO_2). Ambient air quality measurements obtained by KI methods have been designated as "oxidants" in this document. The Federal Reference Method (FRM) for determining whether an area is attaining the current photochemical oxidant standard is an ozone-specific monitoring technique. Its usage for attainment purposes is based on the premise that ozone is the major component of the photochemical oxidant mixture and can be measured as a surrogate (substitute) for oxidants. The FRM eliminates several problems identified in KI methods, including those involved in correcting for the impact of other pollutants and those related to inaccuracies and imprecisions in KI techniques.[6]

Because of the inherent variability of the KI methods, these monitoring instruments must be routinely calibrated with respect to known ozone concentrations. This is true even for controlled greenhouse or field chamber studies in which plants are exposed to purified air to which only ozone has been added. If these procedures are not followed, actual ozone concentrations may be 50-100 percent higher than the measured values.[5] The criteria document has reviewed several studies comparing the KI and FRM measurement techniques in ambient environments. While recognizing the limitations placed on such studies by the imprecisions inherent in the KI methods, the document concluded that properly conducted KI measurements generally indicate levels of oxidant comparable to or slightly higher than levels of ozone as measured by ozone-specific techniques.[7] This conclusion is compatible with the generally established premise that photochemical oxidant mixtures consist predominantly of ozone and lesser amounts of other non-ozone oxidants (such as PAN.)[8]

In view of the above discussion, data obtained in vegetation studies examining controlled ozone exposures or ambient oxidant episodes which stipulate the use of calibrated KI or FRM monitoring methods have for the purposes of this document been considered to be of superior reliability. The analysis of alternative standard levels set forth in subsequent sections has been restricted to such data. However, such well-specified studies are not too plentiful, so this document has for illustrative purposes presented some data from other studies which did not meet this criteria. Studies meeting the superior reliability criteria have been differentiated in this document either expressly or (for convenience) by placing the symbol "(+)" after the concentrations being reported.

Finally, it should be noted that the current oxidant standard and much ambient concentration data are stated on a mass concentration basis (in micrograms per cubic meter, or $\mu g/m^3$), whereas essentially all of the effects data are identified on the basis of molar concentrations (parts per million by volume, or ppm). The relationship between these measurement units is a function of temperature, pressure, and chemical species, but for the purposes of this document conversions between these units were made at standard barometric pressure (101.3 kilopascals) and 25°C and (in the case of ambient measurements) assuming ozone to be the only oxidant present, so that 1 ppm of ozone equals 1960 $\mu g/m^3$.

2. Foliar Injury: Both short-term and long-term controlled exposures of vegetation to ozone have resulted in reductions of growth and yield.[9] However, most of the data discussing vegetative response to ozone, particularly for short-term exposures, is based on visible foliar injury as the measurement of response.[10] Acute leaf injury may result from short-term peak ozone exposures, with some plants developing characteristic patterns of cell destruction (e.g., upper surface fleck in tobacco and stipple in grape). Long-term or intermittent exposures to low ozone levels can produce chronic leaf injury such as chlorosis (loss of chlorophyll) or premature leaf aging (senescence). These symptoms may be confused with those caused by natural aging or other environmental stresses.[11]

The National Academy of Sciences (NAS) has compiled a list[12] classifying some 70 species and cultivars thereof as to their susceptibility to short-term ozone exposures. Excerpts from this list are presented in Table 1. Several important agricultural crops listed (e.g., alfalfa, bean, corn, oats, soybean, and tobacco) have cultivars that are sensitive to ozone damage.

The importance of considering the variation of vegetative response to different ozone exposure levels* in the selection of an ambient air quality standard has been emphasized by several researchers.[13,14] For instance, Jacobson examined this issue in a paper[13] which reviewed the scientific literature and summarized a large amount of data relating visible foliar injury response to short-term ozone exposure levels. These relationships were presented for two types of vegetation (woody plants and agricultural crops) in the form of limiting values which are listed in Table 2. These limiting values depict the range of minimum exposure levels which have been demonstrated to produce foliar injury in a variety of plant species. Exposure levels in excess of the upper limits are likely to injure susceptible species, such as certain bean and tobacco cultivars, while those below the lower limits are unlikely to cause foliar injury.

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*This document uses the term "exposure level" to emphasize that both the concentration and exposure duration must be specified to adequately describe an exposure; it has been attempted to differentiate this concept from that of "dose", which term has been used to indicate the product of concentration and exposure duration.

The data utilized by Jacobson in formulating these limiting values were derived from studies which at least specified the plant species tested, the source of the pollutant, and the concentration and duration of exposure. While these qualifications were a less rigorous set of data reliability criteria than might be desired, they enabled the limiting values so derived to be based on a large amount of data obtained by many different investigators.[13]

Utilizing a somewhat smaller data set than Jacobson, Larsen and Heck[14] have examined the exposure level/vegetative response issue and presented their findings in a manner which is quite suitable for the purposes of evaluating alternative ozone air quality standards. They have summarized the results obtained from experimental short-term fumigations of several species in a mathematical model that quantitatively predicts the extent of foliar injury in specific crops as a function of ozone concentration and exposure duration. This model permits analysis of the standard level to be conducted without placing undue emphasis on results obtained with commercially unimportant cultivars (for instance, Bel W-3 tobacco). Also, by its prediction of the extent of foliar injury associated with a given exposure level, the model permits some quantitative assessment of the severity of damage which could be expected to accompany a given air quality standard. A further advantage of Larsen and Heck's model for use in the analysis of alternative standard levels is the fact that they restricted their evaluation of the model to data of superior reliability.

This model is based on the following assumptions: (1) a constant degree of foliar injury is produced by exposure regimes wherein the pollutant concentration varies in inverse proportion to the exposure duration raised to an exponent, and (2) for a given exposure duration the degree of foliar injury varies with the pollutant concentration in a manner producing a log-normal frequency distribution. The equation describing this model is:

$$c = \left[m_{g_{hr}}\right]\left[s_g\right]^z t^p \qquad (1)$$

where c is the concentration (ppm) expected to produce a degree of foliar injury z standard deviations from 50 percent over an exposure duration of t hours. The other parameters are constants to be determined for a given species and cultivar from the experimental evidence.[14]

This model was evaluated using condensed data obtained from a total of several hundred replicate ozone exposures for 15 different plant species/cultivars which vary considerably in their susceptibility to ozone damage. The presentation of some specific data utilized by Larsen and Heck may be useful for illustrative purposes. Exposure of Roma tomato to 0.075 ppm (+) ozone for 2 and 4 hours produced, respectively, 1 and 10 percent leaf injury as an average for 12 replicate plants.[15] The median injury ratings for 16 replicates of Pinto bean and of Bel W-3 tobacco were 11 and 57 percent, respectively, following exposure to 0.1 ppm* for 4 hours.[14,16] Seven-hour exposures of 4 replicate plants of Cherry Belle radish and Clintland 64 oats to 0.1 ppm (+) resulted in average injury ratings of 39 and 15 percent, respectively.[15]

Using multiple linear regression techniques to analyze the experimental data, Larsen and Heck evaluated the model for each of 15 species/cultivars to determine the parameters for equation (1). Their results are presented graphically in Figure 1 as parallel lines of constant leaf injury on plots of ozone concentration versus exposure duration. A reasonably good fit with the experimental data is demonstrated; each number on the plot gives the median percent injury sustained by a set of plants subjected to the ozone exposure level given by the coordinates of the decimal point of that number.[14]

The leaf injury equation parameters for the 15 cultivars are presented in Table 3, along with the injury threshold concentrations (arbitrarily defined as that concentration producing 1 percent injury) for different exposure durations, as calculated from the equations. The column listing the multiple correlation coefficients for each cultivar's injury equation parameters indicates a reasonably good fit with the data, since all but one coefficient is above 0.88.

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*The principal author of the original study[16] has recommended[17] that the concentrations reported be multiplied by about 1.4 to correct them to neutral buffered KI ozone values, which would make them comparable to the rest of the data used by Larsen and Heck.

A preliminary statistical analysis of this model by EPA[18] on the basis of raw data presented by Larsen and Heck[14] indicated that there is considerable variability in the biological response of individual plants to a given ozone exposure level. For this reason, the model as presented should not be considered sufficiently precise to distinguish between median injury ratings that differ by five percent or less in sets of plants subjected to different exposure levels when the sets are of sizes comparable to those examined by Larsen and Heck. It does seem adequate to indicate injury trends and can probably be relied upon to distinguish statistically significant differences between the median injury ratings of exposed sets when they differ by six to ten percent or more. The lower side of that range would apply when absolute injury ratings are in the vicinity of 10 percent, and the higher side at 30 percent. Since the purpose of this document is to weigh the impact of alternative secondary standard levels, the sort of relative comparison that can be obtained from this model seems adequate, and the model will be used in subsequent sections for that purpose.

3. Growth and Yield Effects: At this point, however, some discussion of the significance of foliar injury is warranted. An examination of Table 1 indicates that for many sensitive crops, such as alfalfa, broccoli, clover, coleus, petunia, spinach, and tobacco, extensive foliar injury could result in considerable economic losses since the foliar portions are economically important parts of these crops. Their marketability might be reduced by the appearance of injured leaves (as, for example, with ornamentals and tobacco),[19] or reductions in crop value might result from reduced biomass production (growth) associated with the leaf injury.[20] Indeed, the latter effect has the potential for crop value reductions even in cases where the leaves are not an economically important part of the plant, as (for example) with beans, corn, radishes, and tomatoes. Table 4 presents data from several studies examining the effects of controlled ozone or ambient oxidant

exposures on leaf injury and biomass production. This summary indicates a broad spectrum of responses: growth and yield reductions with minimal or no foliar injury (radish and alfalfa); extensive foliar injury with no significant effect on crop yield (tomato); and some reasonably good correlations between these parameters (Pinto bean, sweet corn, soybean, and tobacco).

It may be surmised from the above discussion that foliar injury is an imprecise measure of the effect of ozone on plant growth or yield parameters. Nevertheless, the bulk of the data available on short-term ozone exposures to plants presents foliar injury as the response measure. Consequently, it is necessary to utilize this imperfect parameter to evaluate alternative levels of the secondary standard. A question which immediately arises is the degree of foliar injury which will be considered to be of concern. This question has not yet been definitely answered by researchers, but discussions with investigators[21,22,23,24] in this field have provided some enlightenment on the issue. The consensus obtained was that for foliar injury between 5 and 10 percent there is the potential for detectable reductions in growth or yield, depending on the timing of the injury with respect to critical stages in the life cycle (e.g., the time when bean pods are beginning to mature) as well as on other environmental factors which might bear on the plant's ability to recover from the foliar injury.

Since an ozone air pollution episode might occur at any point in a crop's life cycle and might be randomly associated with other detrimental factors, EPA considers foliar injury rates in the range of 5 to 10 percent to be undesirable. Therefore, EPA proposes that the basis for the secondary NAAQS for ozone be to protect against exposures that may be reasonably expected to produce foliar injury within this range for commercially important crops or important indigenous flora. Cultivars that were specially developed to be sensitive to ozone, i.e., Bel W-3 tobacco, will be exempted from this analysis.

Several investigations have examined the effect of ozone exposures on growth and yield parameters, and the information obtained from such studies can provide useful input to the standard-setting analysis. Table 4 presents results of a few studies relating short-term ozone exposures to growth and yield effects, and in addition the following examples appear notable: A 38 percent reduction in root dry weight was produced by exposure of Cherry Belle radish to 0.25 ppm ozone for three hours.[25] Exposure to 0.1 ppm ozone for two hours produced a 9 percent reduction in the average of three growth responses (shoot weight, flower weight, and flower number) of Capri petunia.[26] A 16 percent reduction in leaflet area growth rate was obtained by exposure of Pinto bean to 0.05 ppm ozone for 12 hours.[27]

Long-term exposures to ozone have been experimentally demonstrated to produce growth or yield reductions in several sensitive crops, including radish, soybean, and corn. As noted in Table 4, measurable growth and yield reductions in comparison to controls have been obtained from exposures to levels as low as 0.05 ppm for 6 to 8 hours per day over several weeks. In addition to the studies cited in Table 4, the following examples are noteworthy: A 25 percent reduction in leaf dry weight for Pinto bean was obtained by continuous exposure to 0.05 ppm ozone for five days. After three days exposure, the leaves exhibited premature senescence as measured by loss of green color.[28] Exposure of the Mesa-Sirsa cultivar of alfalfa to 0.05 ppm (+) ozone for 7 hours per day for 68 days produced a 40 percent decrease (average over two harvests) in forage dry weight.[29,30] The criteria document assessed these long-term exposure studies by concluding that significant growth and yield effects could occur if the average ozone concentration exceeds 0.05 ppm beyond 15 days.[31] Based on the evidence cited in its support, this conclusion is for the purposes of this document interpreted to mean 15 consecutive days with maximum 8-hour-average concentrations above 0.05 ppm.

4. Pollutant Interactions and Ambient Exposures: Controlled experimental studies require elimination of unmeasured environmental factors in order to examine the effect of the factor being evaluated (ozone, in the above studies). However, in the ambient environment, plants are exposed not only to ozone but also to other components of the photochemical oxidant pollution mixture (e.g., PAN) or other unrelated pollutants such as SO_2. Only a few controlled experiments have examined the interactive effects of ozone with other pollutants, most of these utilizing SO_2 as the co-pollutant. Mixed results have been found; depending on the species and cultivars examined, the responses have been observed to be additive (not significantly different from the sum of the effects expected from exposure to the given level of each pollutant alone), or synergistic (greater than additive), or antagonistic (less than additive).[32]

At this point a discussion of another important component of the photochemical oxidant mix, PAN, seems to be warranted. It has been reported that on a molar (ppm) basis, PAN injures vegetation at lower exposure levels than ozone does.[33] Controlled exposure of Pinto bean to PAN at 0.02 ppm for 8 hours produced 44 percent injury, and 90 percent injury was induced at 0.04 ppm for 4 hours.[34] The characteristic injury symptoms for PAN are glazing, silvering, or bronzing of the lower surface of the leaves of plants such as spinach, garden beets, Romaine lettuce, and chard.[35] PAN injury can usually be distinguished from ozone injury by the location and type of lesions. The information base on PAN injury to vegetation is much less extensive than that for ozone, but the available evidence suggests that PAN can play an important role in the effects of ambient photochemical oxidant pollution on vegetation.

In order to evaluate the effects of ambient mixtures of photochemical oxidants and other pollutants on vegetation, several studies have compared plants exposed to unfiltered ambient air in greenhouses or field chambers with those grown in filtered air. In multiyear studies of this type in California, significant reductions have been observed in the yields of lemon (32-52 percent),[36] navel orange (54 percent),[36] Zinfandel grape (50-60 percent),[37] and Acala cotton (5-29 percent).[37] In the study of navel orange trees, oxidant concentrations were above 0.10 ppm an average of 148 hours per month from March through October during the growing seasons studied.[36] In similar experiments conducted in Maryland, an average of 49 percent yield reduction was obtained for two sensitive potato cultivars (Haig and Norland) when exposed to oxidant concentrations which were equal to or greater than 0.10 ppm for 11 hours during the growing season.[38] In New York, ambient air field chamber exposures of Tendergreen bean and Fireball 861 VR tomato over their growing seasons reduced the fresh weight yields by 26 and 33 percent, respectively. The foliar injury symptoms which occurred became more extensive and severe with time; they closely resembled those induced by controlled ozone exposures. Hourly average oxidant concentrations of at least 0.10 ppm (+) occurred 125 times during the 99-day experimental period; 0.20 ppm (+) was the maximum hourly average concentration observed.[39]

5. Economic Assessment: Several assessments of the economic losses to agricultural and ornamental vegetation due to ozone and other oxidants have been attempted. Notably, a study by the Stanford Research Institute (SRI)

in 1969 developed an empirical model for assessing vegetative air pollution damage. Expected oxidant levels were evaluated for over 100 study areas across the U.S. and were used to predict foliar injury and resultant economic damage for various vegetation types. The model estimated the national loss due to the effects of ozone and other oxidants on vegetation in 1969 to be $125 million at the farm level. Due to increases in crop values and the general lack of improvement in ozone levels since 1969, these losses could currently approach $300 million annually.[1]

6. Effects on the Natural Environment: Finally, it must be noted that the indigenous vegetation which constitutes the producer component of natural ecosystems[*] may be affected by chronic exposures to ozone and other oxidants. Disruption of the ecosystem structure and function may result, possibly with irreversible repercussions. For example, severe injury has occurred to the conifer forest ecosystem of the San Bernardino Mountains as a result of oxidant pollution transported from the Los Angeles urban area for many years. Of the 640 square kilometers (km^2) in the San Bernardino National Forest that in 1969 had ponderosa pine, Jeffrey pine, and/or white fir as the co-dominant (overstory) vegetation species, 180 and 220 km^2 had sustained heavy and moderate damage,

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[*] A natural ecosystem is a distinct association of plants (producers), animals (consumers), and other biota (decomposers) with the physical environment (e.g., the soil, air, water, and solar energy influx) which controls them.

respectively, in the pine species. An estimated 1.3 million trees were affected, of which 3 percent had died.[41] A station within the heavil damaged area recorded 100 hours in which the total oxidant concentration equalled or exceeded 0.20 ppm (+) during the summer months of 1969, and the air quality appears to have deteriorated further since then.[42] A 2-hectare (5-acre) study plot in an area sustaining moderate damage experienced a 28 percent decrease in Jeffrey pine timber volume between 1952 and 1972. This loss was attributed to the increased susceptibility to insect attack in oxidant-weakened trees, and possibly also to the suppression of radial growth due to oxidant injury. Growth suppression in pine saplings due to ambient oxidant exposure has been demonstrated experimentally.[43] In addition, decreased tree vigor as a result of oxidant injury has been implicated as having detrimental effects on seed production in ponderosa pines. This effect, in conjunction with the habit of preferential seed consumption by small vertebrates such as the gray squirrel, could seriously reduce the reproductive capabilities of ponderosa pine.[44]

Ozone injury to dominant plant species in forest ecosystems is not restricted to California. Ozone pollution has been implicated as a causative agent for a disease of the eastern white pine, post-emergence tipburn, which occurs throughout the range of this species from the Great Lake states to the Appalachian Mountains. Significantly increased injury symptoms were observed in this species at three locales in the Appalachian region of Virginia following a pollution episode in July 1975. Oxidant concentrations were 0.08 ppm (+) or higher during 43 hours of this 9-day period; peak hourly values as high as 0.13 ppm (+) were recorded.[45,46]

It is very difficult to quantify adequately the importance of natural ecosystems to the public welfare and, consequently, to provide monetary estimates of the impacts of oxidant pollution of natural ecosystems. Timber sales from national forests are an obvious but miniscule portion of the benefits obtained from forest ecosystems. There are other benefits which defy monetary evaluation, benefits which relate to the life-support roles of natural ecosystems in maintaining the quality of life on this planet. These include free services such as the purification of air and water, the control of erosion, the regulation of global climate and radiation balances, and the recreational opportunities provided by wilderness areas.

Several impacts of oxidant pollution on natural ecosystems have been discussed, such as decreased timber production and decreased reproductive capabilities of the dominant plants. These impacts may be harbingers of detrimental effects on the life-support roles of these ecosystems, and definitely indicate the potential of oxidant pollution to diminish the economic and recreational values of these natural resources as evaluated from an anthropocentric (man-centered) point of view. Additionally, these impacts have dire implications for non-human inhabitants of these ecosystems, e.g., small vertebrates whose supply of seeds and fruits are diminished. It appears that decline of the dominant Jeffrey pine species in portions of the San Bernardino Mountains is producing changes in ecosystem structure (such as an increase in open areas populated by ozone-resistant shrubs)[47] which may result in increased erosion and changes in the food chain that may affect animal species.[48] It is possible that the disruption of ecosystem structure and function due to oxidant pollution may change the local environmental conditions to an extent that the disruptions become irreversible.

B. Materials Damage:

Ozone has been shown to accelerate aging processes for several classes of materials,particularly elastomers (rubber), textile dyes and fibers, and certain types of paints. In the case of the elastomers, ozone accelerates the development of cracks in several commercially important types of rubber. Several factors influence the ozone cracking phenomenon, such as the chemical nature of the elastomer, degree of tensile stress (strain) sustained by the elastomer, ozone concentration, exposure duration, and temperature. It has been reported that if sensitive rubber is strained slightly (sufficiently to increase its length by 2 to 3 percent) and exposed to concentrations of ozone as low as 0.01 ppm, cracks or cuts will ultimately appear.[49]

Several studies have shown that the cracking rate is strongly correlated with ozone concentration, with one short-term experiment clearly demonstrating a direct proportionality between these parameters. In this study, strips of natural rubber were strained approximately 100 percent. On the average, cracks were first perceived when the ozone dose reached 1.32 ppm-minutes, with an estimated standard deviation of 0.03 ppm-minute. This study evaluated three ozone concentrations: 0.02, 0.25, and 0.45 ppm.[50] The dose-dependent behavior noted in this study implies that the average ozone concentration during an exposure, without regard to the pattern of concentration variations, determines the rate of elastomer cracking. If this interpretation can be applied over long time scales, two sites with equal annual average ozone concentrations would be expected to sustain equal elastomer damage, even if one site were subject to considerably higher short-term peak concentrations than the other.

Long-term exposure studies may be reasonably interpreted to support the preceding conclusions, although there are considerable variations in the data. In one such experiment, thin specimens of a sensitive synthetic (polybutadiene) elastomer were exposed under constant strain to room air during different seasons of the year. Average ozone concentrations were 0.048, 0.042 and 0.024 ppm in the summer, autumn, and winter, respectively. The average dose (and estimated standard deviation thereof) required to induce complete failure in these specimens was 16.6 ± 4.5 ppm-hours. This dose-dependent response indicates that elastomer cracking rates are dependent on the long-term average ozone concentration.[51] Such a deduction is supported by theoretical considerations of the mechanisms of ozone attack on materials. Therefore, it is concluded that long-term (annual) average ozone concentrations determine the extent of elastomer damage.

To protect against ozone cracking, certain substances (anti-ozonants) are generally added to elastomer formulations, and special ozone-resistant elastomer polymers are sometimes used. Such preventive measures are expensive and add considerably to the total economic impact of ozone air pollution. In 1970 a study estimated the nationwide economic impact at the consumer level to be $500 million annually. About $170 million of this total was involved in preventive measures, with the remainder due to premature failure of rubber products.[52] Such an estimate, while demonstrating the seriousness of the problem, does not relate materials effects to ozone exposure levels. In an attempt to provide such a relationship, an equation was developed to present the optimum per capita cost of elastomer damage (i.e., damage prevention measures were balanced against failure costs so as to minimize total costs) as a function of average ozone concentration. This cost function, expressed in 1970 dollars and given with a 25 percent error range, is:

$$\text{Cost, \$/year/person} = (0.88)\,(1 \pm 0.25)\,(\ln \bar{x} - 1) \qquad (2)$$

where $\bar{x}$ is the annual average ozone concentration in micrograms per cubic meter ($\mu g/m^3$).[52]

The effects of ozone on textiles include deterioration of fibers and dyes, but the fading of dyes is the more significant economic factor.[53] Three different types of textile materials have been reported to sustain major economic losses due to ozone fading of dyes: acetate fabrics, polyester-cotton permanent-press fabrics, and nylon carpets.[54] In 1970, the national cost of ozone fading in these textile categories was estimated to be $80 million per year.[55] By analogy with the above elastomer cost function, an equation estimating the cost of ozone damage to textiles and of damage prevention measures has been presented.[56] Expressed in 1970 dollars and given with a 50 percent error range, this equation is:

$$\text{Cost, \$/year/person} = (0.22)(1 \pm 0.5)\,(\ln \bar{x} - 0.74) \qquad (3)$$

for values of $\bar{x}$ above 5.7 $\mu g/m^3$.

Overall costs for paint and coatings damage by ozone have not been estimated. Costs of additional industrial maintenance painting and vinyl coil coating required because of ozone damage have been estimated in a damage function expressed in 1974 dollars.[57] Based only on these two types of damage, the damage function is:

$$\text{Cost, \$/year/person} = \frac{0.0383\ \bar{x}}{1+0.01\ \bar{x}} + \frac{0.00126\ \bar{x}}{1+0.001\ \bar{x}} \qquad (4)$$

where $\bar{x}$ is defined as in equation (2).

The above cost functions for damage and preventive costs associated with ozone effects on elastomers, fabrics, paints, and coatings have been evaluated (at the mid-point of the error range, where applicable) for various annual average ozone concentrations. The results are presented in Table 5. As these cost functions indicate, there is no threshold level for ozone damage to materials. Indeed, the experimental evidence presented in this section regarding the dose-dependent relationship between materials damage and ozone exposure leads one to the conclusion that any nonzero ozone concentration will contribute to the deterioration of sensitive materials if the exposure is sustained long enough The ramifications of this conclusion on the analysis of the standard level and the bearing of natural contributions to ambient ozone levels in the issue of materials damage will be explored in the subsequent sections of this document.

IV. Air Quality Issues

The previous section discussing the experimental evidence of the effects of ozone on vegetation and materials leads directly to issues concerning current ambient levels and the contributions thereto by natural processes (natural background), as well as the matter of which averaging time(s) to choose for setting a secondary standard.

A. Sources and Concentrations of Oxidants in Ambient Air

1. Sources: Ozone levels in the lower atmosphere (troposphere) essentially result from two processes: (a) tropospheric photochemical reactions involving organic and nitrogen oxide precursors, oxygen, and sunlight, and (b) downward transfer of ozone from upper atmospheric (stratospheric) layers into the troposphere. The latter process contributes to the natural background of ozone, and it is possible that photochemical reactions involving naturally emitted precursors may do so also. However, all present evidence indicates that the severe oxidant problems occurring in and around urban areas are preponderantly due to photochemical reactions involving man-made (anthropogenic) precursor emissions.[58] In areas with lesser problems the stratospheric source may be significant, and especially in remote areas that may on occasions be the dominant cause of the ambient ozone levels observed.[59]

2. Urban Oxidant/Ozone Levels: Ambient air concentrations of ozone or oxidants were measured in 1976 at 558 monitoring sites operated by state and local air pollution control agencies and EPA.[60] Table 6 presents 1976 ozone data summaries for 100 sites in the nation's 16 most populous urban areas; only one valid site had its annual second-highest hourly

concentration[*] below the current oxidant standard level of 160 μg/m^3 (approximately 0.08 ppm). Table 7 summarizes oxidant and ozone data from several years' monitoring in 23 urban areas. The annual average concentrations for these sites are presented for comparison with the material effects data in Table 5.

A number of these urban areas have experienced very high levels of oxidant, exceeding 0.3 ppm. Los Angeles, for example, has recorded maximum 1-hour values in excess of 0.6 ppm. Denver, Philadelphia, Houston, and the area just east of New York City have experienced levels above 0.3 ppm. Hourly values above 0.2 ppm have occurred in most of the major urban areas.[61] In addition, excessive ozone concentrations occur quite frequently in urbanized areas, as indicated in Table 6 by the fact that in 8 of the 16 most populous urbanized areas, 20 percent or more of the days in 1976 had hourly values above the current standard level.

3. Rural Ozone Levels: An issue of considerable importance to setting a secondary ozone standard is the ozone air quality in rural areas, since the bulk of the vegetation is in such locales. In recent years research conducted in several rural areas in the eastern and central parts of the nation has indicated that ozone concentrations above the current standard level can occur with a frequency comparable to or even greater than that observed in many urban areas. This is illustrated in Table 8 by data obtained in recent summertime field studies sponsored by EPA. Such elevated ozone levels in rural areas can be almost certainly attributed largely to anthropogenic causes: the transport from urban areas of ozone and/or the photochemical reaction of precursors generated locally or

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[*] The emphasis on the second-highest values is due to the definition of the current oxidant standard as an hourly average concentration not to be exceeded more than once per year. Thus the annual second-highest hourly value determines whether the current standard is attained.

transported from urban areas. The evidence leading to this conclusion includes the correlation of the high ozone levels with increased concentrations of such tracers of man's activities as Freons or acetylene, as well as wind trajectory analyses indicating the prior passage of the rural air over urban sources.[62] The utilization of these and other techniques has enabled researchers to substantiate such phenomena as the intermediate-range transport of ozone plumes up to and exceeding 160 km downwind of urban areas, and the synoptic-scale transport of ozone and its precursors over broad areas (several hundred kilometers in radius) which can occur under appropriate meteorological conditions such as stagnant high pressure systems. The evidence for transport of ozone and other oxidants suggests that most of the oxidant observed in rural areas is due to the influence of upwind urban areas.[63]

4. Natural Background Levels: In the assessment of the extent to which elevated rural ozone levels are due to anthropogenic influences, one useful technique has been to monitor ozone in remote areas in order to determine the natural background levels. Even though remote sites are by definition so far removed from anthropogenic pollutant sources as to make their contamination by such pollutants unlikely, the preceeding discussion indicates that the possibility of anthropogenic influences cannot be summarily discounted even in quite remote areas. Before ascribing a particular ozone level observed at a remote site entirely to natural background, it is necessary to examine the episode with respect to the presence of tracers of man's activities (such as Freons or acetylene) and to conduct wind trajectory analyses to determine whether the air parcel in question had recently passed over urban areas. Nevertheless,

for the purposes of this report "remote" sites will be distinguished from non-remote "rural" sites on the basis of the available evidence that anthropogenic influences play a more important role in the ozone levels observed at rural sites (such as those given in Table 8) than at remote locales.

The 1970 criteria document for photochemical oxidants reported that oxidant concentrations at remote sites ranged from less than 0.01 to about 0.05 ppm (20 to 100 μg/m^3).[64] However, a recent examination[65] of ozone and precursor air quality data at 13 monitoring stations selected to be as remote as possible from anthropogenic sources has indicated that ozone concentrations may occasionally approach and even go above the 0.08 ppm standard level under conditions for which anthropogenic influences are negligible. Such events tend to occur in late winter and early spring (February-April) when the effect of stratospheric transfer into the troposphere is most pronounced, and are more likely at higher elevations. These types of excursions above the standard level were rather infrequent and in fact none occurred at over half of the monitoring sites, with from 6 to 19 months' data at each site. The excursions for which anthropogenic influences could be ruled out were nearly all less than 0.10 ppm, although on one occasion a peak hourly average concentration of 0.20 ppm was reached.

Table 9 indicates maximum hourly and long-term average concentrations observed and the estimated frequency of concentrations above the standard level for the monitoring stations for which long-term data are given in this study. Only three sites had concentrations above 0.10 ppm. Two of these (Fritz Peak, Colorado and White Face Mountain, New York) are frequently subject to long-range transport of anthropogenic pollutants from urban areas despite their nominally remote locations. The preponderance of the excursions above the standard level at these sites can probably be attributed to ozone transport from urban areas. At the third site (Zugspitze, West Germany), the only excursion above the standard level was an episode in which the peak hourly ozone concentration was 0.20 ppm. This episode was indisputably due to an unusually strong penetration of stratospheric ozone (i.e., stratospheric intrusion) to this mountain peak location.[65] The frequency of this type of event is not yet known.[66] A comparison of Tables 8 and 9, particularly with regard to frequency of concentrations above the standard level and the level of maximum hourly average concentrations, provides further support to the conclusion that the bulk of the ozone problem in non-remote rural areas is due to anthropogenic influences.

A further point to be discerned from Table 9 is that the long-term average ozone concentrations at these remote sites varied from 0.028 to 0.044 ppm. This range is somewhat higher than estimates obtained in attempts to quantify stratospheric ozone input to the troposphere through analyses of global circulation patterns. Annual average ground-level ozone concentrations due to stratospheric input have been estimated by such analyses to be in the range of 0.01 to 0.03 ppm. Furthermore, current understanding of the transfer of stratospheric ozone to the troposphere indicates variations with season and latitude such that average ground-level ozone concentrations in the midlatitudes (e.g., the 48 contiguous states) attributable to stratospheric input reach a peak in the winter and spring months. Consequently, the annual average ground-level ozone concentration due to stratospheric input should be higher than the corresponding "smog season" average during the summer months (when the potential for generation of anthropogenic ozone is greatest). Based on these arguments, the criteria document estimated the contribution of stratospheric ozone to the maximum hourly average ground-level concentration during the smog season to be in the range of 0.015 to 0.04 ppm.[67]

Comparison of Tables 7 and 9 indicates that annual average ozone concentrations in urban areas are approximately the same as those in remote sites, even though the maximum hourly concentrations are much higher in urban areas. This seeming paradox can be rationally explained as resulting from the increased rate of nighttime destruction of ozone in urban areas by man-made pollutants such as nitric oxide (NO).[68] This process lowers the nighttime urban ozone concentration practically to zero, whereas ozone destruction processes in remote sites (with minimal concentrations of anthropogenic pollutants) are much less drastic. For this reason the annual average concentrations are comparable even though the maximum hourly values are quite different.

The preceding discussion of natural background ozone levels has emphasized the relatively well-established fact that transfer of stratospheric ozone to lower levels of the atmosphere does occur to an extent that can noticeably affect tropospheric ozone air quality. Another potential source of natural background ozone that is less well defined involves the action of photochemical processes on naturally emitted organic compounds, e.g., terpenes emitted from forested areas. Laboratory and field studies of photochemical reaction processes have demonstrated that terpenes can serve as ozone precursors under optimum conditions, that is, with optimum ratios of the concentrations of organic and nitrogen oxide precursors. However, these optimum ratios do not typically occur in rural areas where the preponderance of natural organic emissions occur. Furthermore, based on extrapolations from laboratory studies, even under optimum conditions for ozone generation no more than 0.001 to 0.002 ppm oxidant/ozone would be predicted to result from ambient terpene concentrations normally observed in forested areas. Under the more typical, non-optimum conditions, the available evidence indicates that terpenes act as ozone scavengers, reacting with and destroying ozone and producing mainly particulate degradation products. The criteria document reviewed the literature available on this subject and concluded that there is no convincing reason to believe that any known natural organic emissions (including terpenes and methane) have an important impact on oxidant/ozone air quality.[69]

5. Levels of Non-Ozone Oxidants: Some discussion of the ambient concentrations of non-ozone oxidant species is merited. Ambient measurements of such oxidants are scant and consist mostly of PAN data. PAN is a highly reactive, unstable compound which must be treated with special precautions, and for these reasons cannot be measured in a routine monitoring program.[70] The data currently available generally indicate that in urban areas PAN concentrations are considerably smaller than those of oxidant or

ozone, but nevertheless are not negligible.[8] Levels in excess of 0.05 ppm have been observed in Los Angeles and elsewhere.[71,34] Ratios of molar (ppm) concentrations of oxidant or ozone to PAN during midday hours have been reported to range from 3/1 to 80/1 in three metropolitan areas. Measurements of ozone and PAN in rural areas near Wilmington, Ohio indicated that absolute concentrations of PAN were lower than those observed in urban areas, with a maximum of 0.004 ppm observed during August 1974. The ratios of ozone to PAN varied from 10/1 to over 150/1.[71] From the wide ranges given in the ratios of ozone to PAN it is obvious that the PAN concentration cannot be predicted from the ozone concentration. These ambient data relationships do not provide conclusive evidence that control efforts aimed at reducing ozone levels (i.e., emission controls for organic and nitrogen oxide precursors) will reduce PAN levels. However, the evidence from laboratory and theoretical studies of photochemical reaction processes definitively indicates that decreases in organic and nitrogen oxide precursor emissions should have greater impacts on ambient PAN than on ambient ozone.[72]

B. Averaging Time Considerations

1. Discussion of Issues: Analysis of the variation of ambient concentrations with averaging times is important in the standard-setting process since effects may vary with intervals of exposure. As has been previously discussed, the effect of ozone on materials appears to be linearly dependent on the dose; this implies that the annual average ozone concentration is the most appropriate indicator of materials damage. However, in the case of vegetation the effects of ozone are not linearly dependent on the dose. In determining the response of vegetation to ozone or oxidants,

concentration is more important than time. A given dose presented to a plant in a short period of time has a greater effect than the same dose applied over a longer period.[73]

The current photochemical oxidants standard level is specified as a one-hour average. Rather than specify different standard levels for different averaging times, it seems prudent from a data-handling point of view to retain the concept of a standard specified for a single averaging time. A one-hour averaging time is sufficiently long to assure accuracy of measurement under conditions of fluctuating atmospheric levels of ozone. Accordingly, EPA proposes to retain the one-hour averaging time for the standard. However, since it has been indicated that plant response is predicated on length of exposure as well as concentration, consideration must be given to the expected variation of ambient ozone concentrations with averaging time in order to assure that the one-hour average standard level is protective of undesirable effects due to exposures sustained over longer averaging times. The following discussion addresses this issue.

2. Prediction of Averaging Time Distributions: The evidence obtained from a considerable amount of air quality data indicates that the maximum observed concentrations decrease as increasingly longer averaging times are evaluated. This is illustrated in Appendix A by plots of annual second-highest ozone concentrations for various averaging times, as reported

for 24 monitoring site-years at several urban locations in the eastern and central parts of the nation. Each plot has been approximately fitted with a straight-line construction of an averaging-time distribution curve. This simplified fitting procedure is a modification of the findings presented by Larsen[74] regarding the relationship between maximum concentrations and averaging times, and is for illustrative purposes only.

Although all the data in Appendix A show a decrease in maximum ozone concentrations with increasing averaging time, there is considerable variability in the rate of decrease. It is necessary to develop a composite of this type of data in order to obtain useful conclusions. Details of the analysis performed for this purpose are given in Appendix B, and are briefly summarized as follows: Ozone measurements from 14 urban monitoring stations (22 site-years) were fitted by Weibull frequency distributions and analyzed to determine the relationships between the distribution parameters for three different averaging times (1,3, and 8 hours). For the 3- and 8-hour averaging times, the data were evaluated for only the 8 and 3 time periods, respectively, that coincide with a calendar day. None of the monitoring stations examined were in compliance with the current oxidant standard, but it was assumed that the relationships between the distribution parameters for different averaging times will remain valid when the standard is attained. These relationships were then applied to a 1-hour ozone concentration frequency distribution believed to describe reasonably well an average urban area meeting the current oxidant standard. For each of the three averaging times, this analysis produced estimates of the concentrations which are expected to be exceeded only once per year for four alternative hourly average ozone standard levels (0.06, 0.08, 0.10, and 0.12 ppm). These estimates are presented in Table B-1. As an example, for an hourly average ozone standard level of 0.08 ppm (157 μg/m^3), the 8-hour average concentration expected to be exceeded only once per year is 0.052 ppm An estimate of the range which might be expected in this value may be obtained by examining the data for the 5 site-years in Appendix A whose annual second-highest hourly average concentrations were below 200 μg/m^3 (0.1 ppm). Assuming that a reduction in the hourly peak values to 0.08 ppm would result in a proportional decrease in the 8-hour-average peaks, a range of annual second-highest 8-hour-average values from 0.047 to 0.064 ppm would be predicted.

3. Synthesis of Averaging Time and Foliar Injury Models: The model proposed by Larsen and Heck[14] for analysis of foliar injury to several plant species can now be examined in the light of exposure levels expected to accompany alternative standard levels. Table 10 presents the results for three averaging times and four alternative hourly average ozone standard levels. It may be readily discerned that in very many instances the 8-hour average concentration expected to be exceeded only once per year is predicted to produce greater foliar injury than the corresponding 1- and 3-hour concentrations. At the 0.06 ppm standard level none of the 15 plant species/cultivars examined is predicted to sustain more than 1 percent injury as a result of short-term exposure levels expected to be exceeded only once per year. For the 0.08 ppm standard level, none of the plants tested except Bel W-3 tobacco is predicted to receive more than 3 percent injury. However, at the 0.10 ppm standard level, several commercially important cultivars (tomato, oats, and

radish) are predicted to sustain injury within the 5 to 10 percent range of concern due to short-term exposure levels expected to be exceeded only once per year. At the 0.12 ppm standard level the injury is expected to be even greater.

In addition to these short-term exposure considerations, the evidence previously presented on long-term exposures is relevant to an analysis of alternative standard levels. The criteria document concluded that significant growth and yield effects could occur if the ozone levels are above 0.05 ppm for 6 to 8 hours per day for 15 consecutive days.[31] Since an 8-hour average concentration of 0.052 ppm is expected to be exceeded only once per year for an hourly average standard level of 0.08 ppm, it appears that growth and yield reductions due to long-term ozone exposures would be more than adequately protected against by that standard level. However, further discussion of this issue in the next section tempers that conclusion somewhat.

It should be noted that the analysis of the variation of maximum concentrations with averaging times relied entirely on ozone measurements obtained in generally urbanized areas. Sufficient data were not available to conduct similar efforts for rural sites downwind of urban areas, but it seems possible that the rate at which maximum ozone concentrations decline with increasing averaging times could be lower in such areas than in metropolitan areas. This hypothesis is based on the fact that, compared with urban areas, rural sites do not have significant sources of man-made pollutants (such as NO) to promote gas-phase ozone scavenging reactions. These reactions, along with other factors such as the daily cycle of ozone formation by photochemical processes, the temporal variations in dispersion conditions, and the scavenging of ozone on surfaces such as soil and vegetation, cause the peak ozone concentrations to decrease with longer averaging times. The conclusion implied by this postulate is that of an urban area and a non-remote rural area which are both meeting a given 1-hour standard level, the rural area would sustain greater injury due to the peak 8-hour exposure. Since the bulk of vegetation is located in rural areas, EPA has attempted to factor the uncertainty raised by this hypothesis into its analysis of alternative hourly average standard levels. However, EPA is soliciting comments as to whether the standard should be set for an averaging time of 8 hours rather than 1 hour in order to remove the uncertainty associated with estimating the ratios of 1-hour to 8-hour values in rural areas.

V. Analysis of Alternative Secondary NAAQS

A. Pertinent Issues

A variety of factors which may be considered by the Administrator in choosing between alternative ozone secondary NAAQS have been discussed in earlier sections of this document, and are briefly summarized as: (1) detrimental effects of ozone on agricultural crops and the natural environment, with repercussions on the benefits derived therefrom by mankind, (2) ozone damage to materials, (3) increased effects due to interaction of ozone with other pollutants, and (4) the transport of anthropogenic photochemical pollutants (either oxidants or their precursors) from urban areas to rural areas. An attempt has been made to weigh these factors in the analyses of alternative ozone NAAQS presented in subsequent sections.

In addition, this document has addressed the issue of the natural background contribution to ambient ozone concentrations. However, EPA does not consider this issue to be relevant to the determination of the level of air quality which is requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of ozone in the ambient air.[75] Consequently, although the magnitude, distribution, and variation of natural background ozone is an important issue in developing regulatory strategies to attain the standard, it is not a pertinent factor in the choice between alternative standard levels.

B. Analysis of Options

1. Change from Deterministic to Statistical Form of Standard: The current standard specifies that the hourly average ozone concentration must not exceed 160 μg/m^3 (approximately 0.08 ppm) more than once per year. As discussed in a companion document,[76] this deterministic form has several

limitations, one of which is the fact that it does not adequately take into account the random nature of meteorological variations. This limitation means that compliance with the standard, and consequently precursor emission control requirements, would be determined on the basis of exceedingly rare adverse weather conditions. The probability of occurrence of such rare conditions can only be dealt with by the utilization of statistical methods. Therefore, EPA is proposing that the standard be expressed in a statistical form. The predictions of foliar injury due to ozone exposures expected to accompany different standard levels given in Table 10 were performed for standards expressed in the statistical form being proposed. Consequently, the effect of this change is included in the analysis of alternative standard levels.

2. Analysis of the Chemical Species Designation of the Standard: The current standard is designated as a photochemical oxidants standard, but the FRM for determining compliance specifically measures ozone and uses it as a surrogate for total oxidants. It is proposed to change the designation of the standard to ozone since that is the chemical species being measured to determine compliance. The predictions of foliar injury given in Table 10 are based on controlled exposures to ozone alone and do not indicate the degree of foliar injury that might occur when plants are exposed to the specified levels of ozone in the ambient air in conjunction with other components of the photochemical oxidants category, such as PAN. Controlled exposures of plants to PAN have indicated that it is a potent injurious agent, and injury symptoms characteristic of PAN have been noted in ambient air exposures, particularly in California.

However, EPA does not propose to set a PAN secondary air quality standard at this time for several reasons. In the first place, there is no satisfactory technique available for use in routine PAN air monitoring programs. Secondly, the evidence from laboratory and theoretical studies of photochemical reaction processes definitively indicates that decreases in organic and nitrogen oxide precursor emissions as a result of ozone control strategies should have even greater impacts on ambient PAN levels than on ambient ozone.[72] The possible interactive effect of ozone with residual levels of PAN remaining after attainment of an alternative ozone standard has been considered by EPA (along with interaction with other pollutants) in the choice of the proposed ozone standard level, as discussed below.

3. Analysis of Alternative Standard Levels for Vegetative Effects: Four alternative hourly average standard levels were selected for analysis: 0.06, 0.08, 0.10, and 0.12 ppm (approximately 120, 160, 200, and 240 $\mu g/m^3$). The levels were chosen to permit analysis of the impacts on the public welfare from either raising or lowering the current standard level (160 $\mu g/m^3$). In each case, the standard was expressed in a statistical form such that the standard would be attained if the expected number of hours per calendar year with concentrations above the standard level were less than or equal to one.

As was discussed in previous sections, EPA has concluded that protection of the public welfare requires prevention of short-term ozone exposures which may be reasonably expected to produce injury ratings within the range of 5 to 10 percent in commercially important crops or important indigenous flora. This is based on the best-judgment estimates of researchers in this field that such injury ratings could produce detectable reductions in growth or yield, depending on the timing of the injury and other environmental factors. Furthermore, long-term exposure patterns wherein the ozone levels exceed 0.05 ppm for 6 to 8 hours per day for 15 consecutive days could produce significant growth and yield effects. These two analytical criteria provide the bases for evaluating alternative standard levels with regard to their effects on vegetation.

With respect to the first criteria, a mathematical model was used to summarize for several crops the experimental evidence which depicts the foliar injury response to various short-term exposure levels. This model facilitated the extrapolation of direct experimental results over averaging times in the range of 0.5 to 8 hours. This permitted evaluation of particular exposure levels for which experimental evidence was lacking but which were critical in distinguishing between certain of the alternative standard levels. As presented in Table 10, the model's predictions of the extent of foliar injury at various exposure levels were combined with estimates of the short-term exposure levels expected to accompany alternative hourly average standards.

These air quality estimates were based on an analysis (given in Appendix B) of the variation in short-term peak ozone concentrations with different averaging times which was judged to be an "average" for several urban locations approaching or attaining the current standard. Admittedly it would be more relevant to the issue of protecting vegetation to analyze such variations for rural locations; however, those relationships are presently not quantified. Nevertheless, it does seem plausible that those relationships may be such that higher 8-hour-average peak concentrations would result at a rural site than at an urban site if both were attaining the same hourly average standard (due to the higher urban levels of ozone-scavenging anthropogenic pollutants, such as NO). The significance of this uncertainty can be seen in the fact that in practically each case examined in Table 10, the 8-hour exposure is predicted to produce more injury than the shorter exposure times.

With respect to the second criteria, the analysis in Appendix B was also used to estimate long-term exposure patterns expected to accompany alternative hourly average standard levels. This analysis contains an inherent bias towards overestimating the long-term impacts of such standards.

The alternative standard level of 0.06 ppm is predicted to protect all of the 15 plant species/cultivars examined in Table 10 from short-term injury ratings above 1 percent. Appendix B indicates that the peak 8-hour concentration is expected to be less than 0.05 ppm. This standard level appears to be stricter than is required to protect the public welfare.

A 0.12 ppm standard level is predicted to produce short-term injury ratings within or exceeding the range of concern for several commercially important cultivars. Cherry Belle radish and Roma tomato are predicted to sustain 12 and 19 percent injury due to the 8-hour average concentration which is expected to be exceeded only once per year for this hourly average standard. In addition, there are direct experimental results in the range of exposure levels expected for this standard; these provide reasonably good corroboration of the model's predictions. Finally, Appendix B indicates that the number of 8-hour average concentrations above 0.05 ppm is expected to be 31 per year. Clearly, a 0.12 ppm standard level would not be sufficiently protective of the public welfare, even at the "average" urban site analyzed in Table 10 and Appendix B.

The analysis of the remaining alternatives, 0.08 and 0.10 ppm, is somewhat more difficult than for the preceding cases. The initial evaluation of these options with respect to the two analytical criteria presented earlier produced conflicting results, as given below.

A 0.08 ppm standard level is predicted to protect all commercially important cultivars examined in Table 10 from short-term injury ratings above 3 percent. Appendix B indicates that the number of 8-hour average concentrations above 0.05 ppm is expected to be 2 per year.

Short-term ozone exposures expected to accompany a 0.10 ppm standard level are predicted to produce injury ratings within the 5 to 10 percent range of concern for some commercially important cultivars (specifically, tomato, oats, and radish cultivars). Appendix B indicates that the number of 8-hour average concentrations above 0.05 ppm is expected to be 10 per year.

With respect to the first criteria, a 0.08 ppm standard seems to be adequate whereas a 0.10 ppm standard does not. But applying the second criteria indicates that both standard levels are adequate. This conflict has been resolved in favor of the 0.08 ppm option according to the following rationale: First, use of an "average" urban site as the basis for the air quality estimates introduces uncertainty with respect to the possibility that higher 8-hour-average concentrations may occur at a rural site than at an urban site when both are attaining the same hourly average standard. Second, another uncertainty in the air quality estimates is provided by the fact that, for 3- and 8-hour averaging times, the data were evaluated for only the 8 and 3 time periods, respectively, that coincide with a calendar day. If the data were analyzed so as to examine all possible 3- and 8-hour periods (i.e., a "running average" analysis), it seems likely that higher 3- and especially 8-hour-average peaks would be associated with a given hourly average standard. Third, both the foliar injury model utilized in Table 10 and the second analytical criteria are based on studies examining controlled exposures of plants to clean air to which only ozone had been added. However, as discussed earlier there have been studies which have demonstrated for some species a synergistic interaction between ozone and other pollutants.

These considerations indicate that the analyses in Table 10 and Appendix B may be underestimating the impacts of the hourly standards examined. Contravening the above conclusion is the aforementioned bias in the analysis of long-term exposure patterns, so that the long-term impacts associated with these standards may be overestimated. Balancing the significance of these uncertainties, EPA considers that the prudent choice for the secondary NAAQS for ozone is an hourly average concentration of 0.08 ppm.

This document has cited evidence[65] that hourly average concentrations above 0.08 ppm may occasionally occur in situations when anthropogenic influences are negligible. In that sense, a 0.08 ppm hourly average standard level may be described as being within the range of natural background. However, these situations are rather infrequent and tend to occur in late winter and early spring (February through April) when the effect of stratospheric transfer into the troposphere is most pronounced, and are more likely to occur at higher elevations. Stratospheric ozone transfer appears to be considerably reduced during the summer months, which is the time when photochemical processes for generating ozone are at a maximum (and when vegetation is at the peak of its physiological activity). Thus the high oxidant levels seen in the summer months when there is greater risk of vegetative damage appear to have their origin predominantly in photochemical processes acting on anthropogenic precursor emissions.

Problems related to excursions above the standard level because of stratospheric ozone transfer to the lower atmosphere may be satisfactorily resolved, then, by making allowances for such occurrences in the implementation of the standard. Thus, as EPA has suggested in a recent technical paper,[77] excursions above the standard level which can be identified with a stratospheric intrusion should not be considered in developing regulatory control strategies.

4. Analysis of Alternative Standard Levels for Materials Effects: As previously discussed, the rate at which ozone accelerates the aging processes of materials depends on the annual average ozone concentration. It seems reasonable that a lower short-term (hourly average) standard level would result in a lower annual average concentration, but this conclusion is brought into question by the fact that urban and remote areas have comparable annual average concentrations even though short-term peaks are considerably higher in urban areas (compare Tables 7 and 9). This anomalous situation is rationally explained as resulting from the increased nighttime ozone destruction rates in the urban areas due to the ability of anthropogenic pollutants (particularly NO) to efficiently scavenge ozone.[68]

Despite this uncertain correlation between short-term peak and long-term average ozone concentrations when comparing different ambient environments (that is, urban versus remote areas), it seems intuitively obvious that for a given type of ambient environment reductions in short-term peaks would result in lower annual averages. Therefore, it may be concluded that ozone control measures in urban areas should reduce annual average ozone levels, and hence reduce the costs of materials damage in a manner suggested by Table 5. As has been noted previously, there is no threshold level below which materials damage will not occur; exposure of sensitive materials to any nonzero concentration of ozone (including natural background levels) will produce effects if the exposure duration is sufficiently long. For the above reasons, no effects-based rationale can be offered to decide the level of the secondary standard needed to protect materials. Consequently, it is proposed that the level of the secondary standard be based on the protection of vegetation.

C. Conclusion

EPA proposes to set the ozone secondary NAAQS at 0.080 ppm (157 μg/m^3) for a 1-hour averaging time. This proposal involves a slight change in the mass concentration expression of the current standard level (160 to 157 μg/m^3) due to restating the standard on a molar concentration (ppm) basis. Another proposed alteration is that the chemical designation of the standard be changed from photochemical oxidants to ozone. Furthermore, it is proposed that the standard be stated in a statistical format. Thus, the proposed standard will be attained when the expected number of hours per calendar year with concentrations above 0.080 ppm (157 μg/m^3) is equal to or less than one. EPA concludes that this secondary NAAQS is requisite to protect the public welfare from any known or anticipated adverse effects on vegetation due to the presence of ozone in the ambient air. This NAAQS is believed to provide considerable protection from the effects of ozone on materials, but no standard level (other than zero) could be said to be completely protective. The slight acceleration in aging processes of materials which occurs at the proposed NAAQS is judged by EPA not to be significant or adverse.

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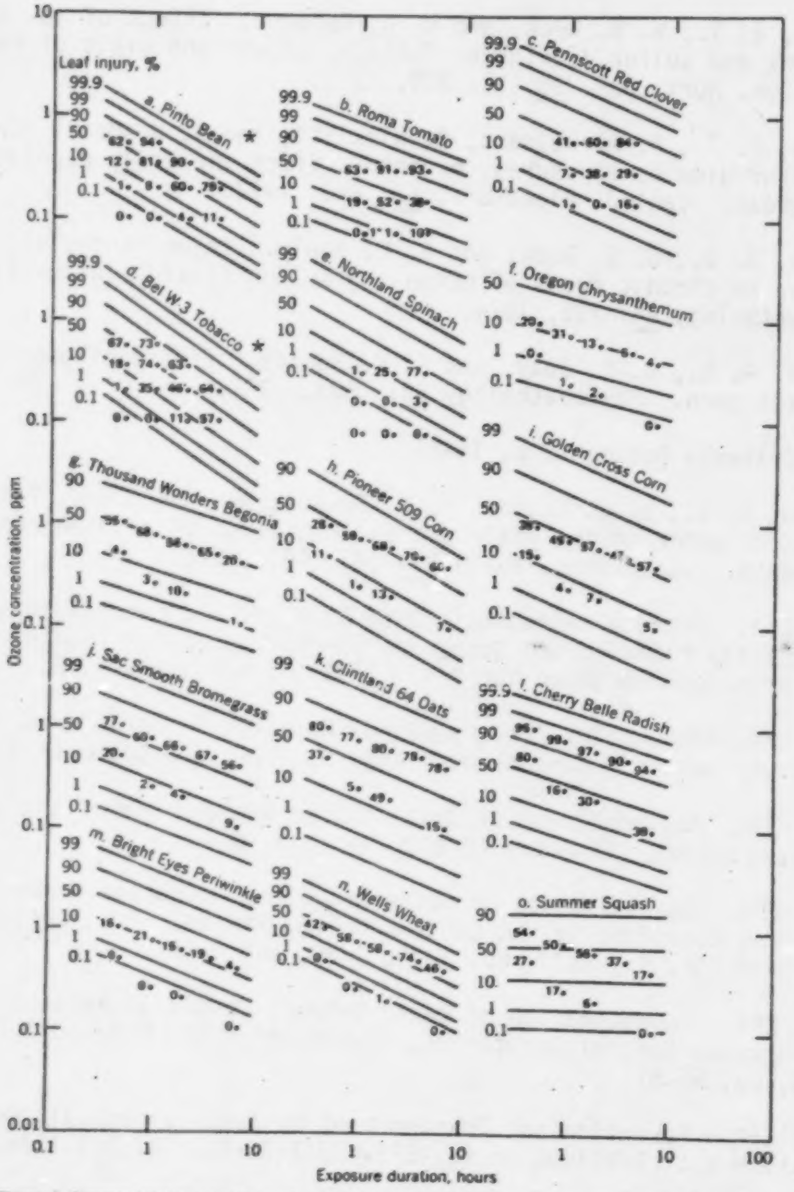

Figure 1. Percent leaf injury in fifteen plant species exposed to various ozone concentrations for various durations.

Reprinted with permission from Larsen and Heck[14]

*The concentration axes for these two cultivars should be multiplied by 1.4 per the recommendation of W. W. Heck.[17]

Table 1 Selected Vegetation Genera and Species Grouped by Sensitivity to Ozone[12]

Sensitive (total 28 species)	Intermediate (total 41 species)	Resistant (total 42 species)
Alfalfa (6)[a]	Alfalfa (9)	Alfalfa (3)
Bean (4)	Bean (5)	Bean (5)
Broccoli (1)	Beet (1)	Chrysanthemum (39)
Chrysanthemum (6)	Cabbage (1)	Clover (1)
Clover (1)	Chrysanthemum (13)	Corn (1)
Coleus (1)	Clover (4)	Cotton (2)
Corn (1)	Coleus (1)	Grass (3)
Grass (6)	Corn (2)	Lettuce (8)
Oats (6)	Grass (10)	Oats (1)
Petunia (2)	Lettuce (1)	Onion (1)
Radish (5)	Oats (5)	Petunia (16)
Soybean (14)	Onion (1)	Soybean (6)
Spinach (4)	Petunia (1)	Spinach (1)
Tobacco (35)	Radish (6)	Tobacco (1)
Tomato (7)	Soybean (19)	Tomato (3)
	Spinach (3)	
	Tobacco (12)	
	Tomato (6)	
	Wheat (1)	

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[a] Numbers in parentheses ( ) are the numbers of varieties of the species for which reports of ozone response were reviewed in the NAS report.[12]

Table 2 Limiting Values for Foliar Injury by Ozone[13]

Averaging Time, Hours	Ozone Concentration, $\mu g/m^3$ (ppm)			
	Agricultural Crops		Trees and Shrubs	
	Lower Limits	Upper Limits	Lower Limits	Upper Limits
0.5	400 (0.20)	800 (0.41)		
1	200 (0.10)	500 (0.26)	400 (0.20)	1000 (0.51)
2	140 (0.07)	300 (0.15)	200 (0.10)	500 (0.26)
4	75*(0.04)	180 (0.09)	120 (0.06)	340 (0.17)
8	40*(0.02)	100 (0.05)	80*(0.04)	200 (0.10)

*Although these values appear in figures depicting limiting values for foliar injury, the author stated that limiting values at concentrations of O_3 below 100 ug/m^3 (0.05 ppm) are not useful because of inaccuracies in measurements. He further stated that much of the data utilized in formulating these limiting values was derived from KI monitoring methods that if uncalibrated would tend to underestimate the actual concentrations by as much as 50 percent. For many of the studies utilized, calibration procedures were not specified.

TABLE 3 Calculated Injury Parameters for Plants Exposed to Ozone[a]

Pollutant and Plant	Calculated Injury Threshold[b], ppm, for Exposure of			Leaf Injury Equation[c] Parameters			Multiple Correl. Coeff.	Injury Conc. Ratio, median/threshold
	1 hr	3 hr	8 hr	$m_{g\ \mathrm{hr}}$	s_g	p		
Ozone								
a. Bean, Pinto *	0.13	0.07	0.04	0.31	1.44	−0.57	0.98	2.3
b. Tomato, Roma	0.09	0.06	0.04	0.24	1.53	−0.35	0.98	2.7
c. Clover, Penscott Red	0.20	0.12	0.08	0.65	1.68	−0.43	0.89	3.3
d. Tobacco, Bel W-3*	0.11	0.05	0.03	0.34	1.60	−0.68	0.93	3.0
e. Spinach, Northland	0.24	0.13	0.08	0.72	1.60	−0.55	0.89	3.0
f. Chrysanthemum, Oregon	0.36	0.26	0.20	1.79	2.00	−0.27	0.76	5.0
g. Begonia, Thous. Wonders	0.18	0.13	0.10	0.76	1.85	−0.31	0.90	4.2
h. Corn, Pioneer 509	0.18	0.10	0.05	0.80	1.91	−0.57	0.94	4.5
i. Corn, Golden Cross	0.15	0.09	0.06	0.83	2.11	−0.44	0.99	5.7
j. Bromegrass, Sac Smooth	0.16	0.11	0.07	0.64	1.80	−0.38	0.95	3.9
k. Oats, Clintland 64	0.09	0.06	0.04	0.47	2.02	−0.41	0.91	5.1
l. Radish, Cherry Belle	0.08	0.06	0.04	0.29	1.72	−0.32	0.93	3.5
m. Periwinkle, Bright Eyes	0.48	0.31	0.21	1.37	1.57	−0.40	0.94	2.8
n. Wheat, Wells	0.39	0.23	0.14	0.83	1.3	−0.4	0.94	2.2
o. Squash, Summer	0.17	0.17	0.17	0.70	1.83	−0.01	0.96	4.1

[a] Reprinted with permission from Larsen and Heck.[14]

[b] The injury threshold is arbitrarily defined here as 1% leaf injury in the median plant of an exposed set.

[c] $c = m_{g\ \mathrm{hr}} s_g^{z} t^{p}$.

*The concentrations given as injury thresholds for these cultivars should be multiplied by 1.4 per the recommendation of Heck.[17]

Table 4

Growth and Yield Responses of Plants to Ozone Exposures, Compared with Foliar Injury Response

Plant species & cultivar (cv.)	O_3 concentration, ppm[a]	Exposure pattern: Number of hours(h), days(d), & weeks(w)	Plant growth or yield response, % reduction from control	Foliar injury response, % increase over control	Reference
Alfalfa, cv. Vernal	0.05 (+)	8h/d, 5d/w, 12w	12##, foliage dry wt; 22##, root dry wt;	0	30,79,80
Bean, cv. Pinto	0.30	0.5h/d, 14d	11#, leaf dry wt; 14#, stem dry wt; 23#, root dry wt.	22[b]	81
	0.30	1h/d, 14d	40#, leaf dry wt; 57#, stem dry wt; 65#, root dry wt;	82[b]	
	0.30	2h/d, 14d	70#, leaf dry wt; 80#, stem dry wt; 83#, root dry wt;	93[b]	
	0.30	3h/d, 14d	76#, leaf dry wt; 85#, stem dry wt; 88#, root dry wt;	90[b]	
Cucumber, cv. Ohio Mosiac	1.0 1.0	1h 4h	19#, top dry wt; 37#, top dry wt;	1* 18#	82
Onion, cv. Spartan Era	1.0 1.0	1h 4h	21#, plant dry wt; 48#, plant dry wt;	2* 6*	82
Radish, cv. Cherry Belle	0.05(+)	8h/d, 5d/w, 5w	10##, leaf dry wt; 50##, root dry wt;	1	83
Radish, cv. Cherry Belle	0.15 (+)	4h	No significant effect	13	
	0.45 (+)	4h	33##, foliage dry wt; 77##, root dry wt;	80	30,79
Soybean cv. Hood and Dare	0.05 (+)	8h/d, 5d/w, 3w	2*, top fresh wt; 3*, root fresh wt;	8#	
	0.10 (+)	8 h/d, 5d/w, 3w	21#, top fresh wt; 24#, root fresh wt;	19#	84
Soybean, cv. Dare	0.05 (+)	6h/d, 133d	3*, seed yield; 22*, plant fresh wt;	19#	85
	0.10 (+)	6h/d, 133d	55#, seed yield; 65#, plant fresh wt;	37#	
Sweet corn, cv. Golden Midget	0.05 (+) 0.10 (+)	6h/d, 64d 6h/d, 64d	9*, kernel dry wt; 45#, kernel dry wt;	14# 25#	86,87
Tobacco, cv. Bel W-3	ambient: often >0.05ppm(+)	48d	22#, leaf fresh wt;	17#	17,20
Tobacco, cv. Bel W-3	0.05 (+)	8h/d, 5d/w, 4w	1*, leaf dry wt; 30##, stem dry wt; 42##, root dry wt;	8	30,79
Tobacco, cv. Burley-21	0.05 (+)	8h/d, 5d/w, 4w	No significant reductions	trace	30,79
Tomato, cv. H-11	0.20(+)	2.5h/d, 3d/w, 15w	1**, fruit yield; 32##, top dry wt; 11**, root dry wt;	extensive, considerable amount of defoliation	88
	0.35(+)	2.5 h/d, 3d/w, 15w	45##, fruit yield; 72##, top dry wt; 59##, root dry wt;	extensive, almost completely defoliated	

*No statistically significant difference from controls, at the 5% confidence level

**No statistically significant difference from controls, at the 1% confidence level

#Statistically significant difference from controls, at the 5% confidence level

##Statistically significant difference from controls, at the 1% confidence level.

[a] The symbol (+) indicates that the reference specified both the monitoring method and the calibration technique.

[b] These data are not presented in reference 81, but were derived from information contained therein.

Table 5 Approximate Annual Per-Capita Materials Damage Costs
For Various Annual Average Ozone Concentrations

Annual Average Ozone Concentration µg/m^3 (ppm)	Costs, $/year/person		
	Elastomers (1970 dollars)	Fabrics (1970 dollars)	Paints and Coatings (1974 dollars)
10 (0.005)	1.15	0.34	0.36
20 (0.010)	1.76	0.50	0.66
30 (0.015)	2.11	0.59	0.92
40 (0.020)	2.37	0.65	1.14
50 (0.026)	2.56	0.70	1.34
60 (0.031)	2.72	0.74	1.51
70 (0.036)	2.86	0.77	1.66
80 (0.041)	2.98	0.80	1.80
90 (0.046)	3.08	0.83	1.92
100 (0.051)	3.17	0.85	2.03

Table 8. Ozone Data from Air Quality Control Regions (AQCR)

Containing the 16 Most Populous Urbanized Areas of the U.S., 1976 [89]

ACQR	Total Number of valid sites[a]	Number of sites with 2nd max. hourly value above standard level[b]	Range of 2nd max. hourly values, μg/m^3 (ppm)	% days with hourly values above standard level at the worst site [c]
New Jersey - New York - Connecticut	2	2	447-470 (0.23-0.24)	29
Metropolitan Los Angeles	21	20	137-706 (0.07-0.36)	55
Metropolitan Chicago	11	11	186-529 (0.09-0.27)	10
Metropolitan Philadelphia	10	10	294-412 (0.15-0.21)	19
Metropolitan Detroit-Port Huron	2	2	347-367 (0.18-0.19)	10
San Francisco Bay Area	14	14	196-333 (0.10-0.17)	24
Metropolitan Boston	2	2	314-345 (0.16-0.18)	23
National Capital	11	11	284-539 (0.14-0.27)	17
Greater Metropolitan Cleveland	4	4	222-345 (0.11-0.18)	28
Metropolitan St. Louis	8	8	198-418 (0.10-0.21)	13
Southwest Pennsylvania	0	-	-	-
Minneapolis - St. Paul	0	-	-	-
Metropolitan Houston-Galveston	4	4	365-523 (0.19-0.27)	34
Metropolitan Baltimore	2	2	314-353 (0.16-0.18)	9
Metropolitan Dallas - Fort Worth	2	2	321-353 (0.16-0.18)	20
Southeastern Wisconsin	7	7	198-504 (0.10-0.26)	25

[a] Only sites having a minimum of 4000 hourly observations were included in this summary.

[b] The photochemical oxidant standard is a one-hour average of 160 μg/m^3 (0.082 ppm) of ozone not to be exceeded more than once per year.

[c] The worst site is defined as the site having the highest percentage of days with hourly values above the standard level.

Table 7. Oxidant Levels in 23 Urban Areas of the U.S., 1964-1976[a], [90,91]

Location	Year	% Data Collected	Annual Second Highest 1-Hour Value, µg/m^3 (ppm)	Annual Average Concentration µg/m^3 (ppm)
Camden, NJ	1973	68	376 (0.19)	44 (0.022)
	1974	90	366 (0.19)	40 (0.020)
	1975	63	505 (0.26)	38 (0.019)
Corpus Christi, TX	1974	80	241 (0.12)	41 (0.021)
	1975	70	241 (0.12)	44 (0.022)
Des Moines, IA	1975	90	192 (0.10)	47 (0.024)
	1975	72	199 (0.10)	66 (0.034)
Louisville, KY	1973	89	362 (0.18)	18 (0.009)
	1974	97	186 (0.09)	18 (0.009)
	1975	99	352 (0.18)	23 (0.012)
Mamaroneck, NY	1973	64	309 (0.16)	26 (0.013)
	1974	94	313 (0.16)	27 (0.014)
	1975	84	258 (0.13)	23 (0.012)
Memphis, TN	1974	95	225 (0.11)	38 (0.019)
	1975	91	254 (0.13)	47 (0.024)
Newport, KY	1973	77	305 (0.16)	41 (0.021)
	1974	95	297 (0.15)	30 (0.015)
	1975	92	321 (0.16)	34 (0.017)
Omaha, NE	1974	90	166 (0.08)	32 (0.016)
	1975	83	225 (0.11)	53 (0.027)
Racine, WI	1974	95	562 (0.29)	50 (0.026)
Richland Co., SC	1973	65	155 (0.08)	30 (0.015)
	1974	94	270 (0.14)	41 (0.021)
	1975	98	245 (0.13)	40 (0.020)
Kansas City, KS	1973	97	130 (0.07)	24 (0.012)
	1975	95	160 (0.08)	19 (0.010)
Pasadena, CA	1964-65	N/A[b]	950 (0.48)*	82 (0.042)
Los Angeles, CA	"	N/A	840 (0.43)*	71 (0.036)
San Diego, CA	"	N/A	440 (0.22)*	71 (0.036)
Denver, CO	1964-65	N/A	440 (0.22)*	71 (0.036)
St. Louis, MO	"	N/A	360 (0.18)*	61 (0.031)
Philadelphia, PA	"	N/A	570 (0.29)*	51 (0.026)
Sacramento, CA	1964-65	N/A	400 (0.20)*	59 (0.030)
Cincinnati, OH	"	N/A	280 (0.14)*	59 (0.030)
Santa Barbara, CA	"	N/A	310 (0.16)*	71 (0.036)
Washington, DC	1964-65	N/A	310 (0.16)*	57 (0.029)
San Francisco, CA	"	N/A	220 (0.11)*	37 (0.019)
Chicago, IL	"	N/A	250 (0.13)*	55 (0.028)

[a] All data in this table obtained after 1970 were measured by ozone-specific techniques. Earlier data measured total oxidants. Also, post-1970 data were obtained from sites having valid data for at least 60 percent of the hours in the year; consequently, the sites presented in this table may not have recorded the maximum annual second-highest hourly values for their respective cities.

[b] Not available

*Estimated from frequency distribution analyses.

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Table 8. Summary of Ozone Data for Rural and Urban Sites in the Eastern and Central U.S., 1973-1975 [92,93,94]

Location	Maximum Hourly Avg. Concentration, µg/m³ (ppm)	Avg. Concen. over Period Examined, µg/m³ (ppm)	% Days with Hourly Values Above Level of Standard	Hours Above Standard Level	% Hours Above Standard Level
June 26 - September 30, 1973: Rural Sites					
McHenry, MD	360 (0.18)	149 (0.076)	78	599	37
Kane, PA	310 (0.16)	130 (0.066)	65	635	30
Coshoctan, OH	350 (0.18)	112 (0.057)	46	350	20
Lewisburg, WV	280 (0.14)	105 (0.054)	39	253	15
June 14 - August 31, 1974: Rural Sites					
Wilmington, OH	370 (0.19)	103 (0.053)	58	259	14.9
McConnelsville, OH	330 (0.17)	102 (0.052)	56	239	13.3
Wooster, OH	330 (0.17)	94 (0.048)	55	262	14.0
McHenry, MD	330 (0.17)	113 (0.058)	43	262	13.0
DuBois, PA	400 (0.20)	112 (0.057)	54	341	20.5
June 14 - August 31, 1974: Urban Sites					
Canton, OH	280 (0.14)	71 (0.036)	44	148	8.0
Cincinnati, OH	360 (0.18)	49 (0.025)	20	54	3.5
Cleveland, OH	270 (0.14)	62 (0.032)	26	51	3.0
Columbus, OH	340 (0.17)	65 (0.033)	27	113	5.8
Dayton, OH	260 (0.13)	71 (0.036)	35	114	7.2
Pittsburgh, PA	300 (0.15)	56 (0.029)	37	106	6.5
June 27 - September 30, 1975: Rural Sites					
Bradford, PA	248 (0.13)	81 (0.041)	18.5	100	4.3
Lewisburg, WV	225 (0.11)	76 (0.039)	11.1	59	2.5
Creston, IA	245 (0.12)	70 (0.036)	7.9	17	0.8
DeRidder, LA[a]	256 (0.13)	61 (0.031)	8.0	38	1.3
Poynette, WI	243 (0.12)	76 (0.039)	21.7	121	5.0
Port O'Connor, TX	259 (0.13)	55 (0.028)	12.4	99	3.4
June 1 - September 30, 1975: Urban Sites					
Pittsburgh, PA	490 (0.25)	60 (0.031)	34.6	227	8.0
Columbus, OH	196 (0.10)	44 (0.022)	11.6	43	1.5
Cedar Rapids, IA	180 (0.09)	50 (0.026)	0.9	6	0.2
Des Moines, IA	196 (0.10)	73 (0.037)	20.9	124	4.9
Omaha, NE	216 (0.11)	71 (0.036)	20.1	64	3.6
Nederland, TX	380 (0.19)	55 (0.028)	33.6	138	5.1
Austin, TX	206 (0.11)	49 (0.025)	9.6	19	0.8
Houston, TX	629 (0.32)	51 (0.026)	37.6	141	6.7

[a] Data obtained for this site through October 31, 1975.

TABLE 9

Ozone Air Quality in Remote Locations.[65]

Station Number	Location	Elevation Above Mean Sea Level, m	Extent of Data, Months (Years of Observation)	Avg. Concen. over Period Examined, μg/m³ (ppm)[a]	Maximum 1-hour Average Ozone Concentration, μg/m³ (ppm)	Month in which Max. 1-hr. Value Occurred	Number of Days with Hours above Standard Level	Estimated % Days with Hours above Standard Level[a]
1	Quillayute, WA	62	19 (1974-75)	55 (0.028)	120 (0.063)	April	0	0
2	McRae, MT	975	15 (1974-75)	77 (0.039)	160 (0.080)	March, June	0	0
3	BN Site, MT	1082	10 (1975-76)	86 (0.044)	180 (0.093)	April	5	<1.9
4a	White River, UT	1590-1625	16 (1974-76)	75 (0.038)	190 (0.096)	May	N/A[b]	N/A
4b			16 (1974-76)	71 (0.036)	150 (0.076)	May	0	0
4c			18 (1974-76)	67 (0.034)	150 (0.076)	March	0	0
5a	Rio Blanco, CO	1900	19 (1974-76)	55 (0.028)	160 (0.080)	June	0	0
5b		2100	19 (1974-76)	55 (0.028)	150 (0.078)	June	0	0
6	Fritz Peak, CO[c]	2730	9 (1975)	73 (0.037)	228 (0.116)	August	7	3
7	Converse Co., WY	N/A	6 (1974)	84 (0.043)	150 (0.076)	June	0	0
8	White Face Mtn., NY[c]	1510	23 (1974-76)	61 (0.031)	212 (0.108)	May	19	3
9	Mauna Loa, HI	3400	24 (1974-75)	67 (0.034)	190 (0.095)	July	6	1
10	Zugspitze, West Germany	3000	21 (1974-76)	59 (0.030)	385 (0.196)	January	2	0.4

[a] These data are not presented in the reference; they were derived from data in the reference after consultation with one of the authors.[95]

[b] Not available

[c] These sites, although nominally remote, are frequently subject to contamination due to long-range transport from urban areas.

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Table 10

Predicted Median Foliar Injury (Percent) due to Ozone Exposures Expected to be Exceeded Only Once per Year for Different Standard Levels, After Larsen and Heck[14]

Plant species, cultivar	Hourly average standard level, ppm ($\mu g/m^3$)											
	0.06 (118)			0.08 (157)			0.10 (196)			0.12 (235)		
	Exposure levels expected to be exceeded only once/year, ppm x hr											
	0.060 x 1	0.052 x 3	0.039 x 8	0.080 x 1	0.069 x 3	0.052 x 8	0.100 x 1	0.086 x 3	0.065 x 8	0.120 x 1	0.104 x 3	0.078 x 8
Bean, Pinto[a]	0	0	0	0	0	1	0	0	3	0	1	7
Tomato, Roma	0	0	1	0	2	3	2	7	9	5	15	19
Clover, Penscott Red	0	0	0	0	0	0	0	0	0	0	0	1
Tobacco, Bel W-3[a]	0	0	1	0	1	4	0	2	11	0	5	20
Spinach, Northland	0	0	0	0	0	0	0	0	0	0	0	1
Chrysanthemum, Oregon	0	0	0	0	0	0	0	0	0	0	0	0
Begonia, Thous. Wonders	0	0	0	0	0	0	0	0	0	0	0	0
Corn, Pioneer 509	0	0	0	0	0	1	0	1	2	0	1	4
Corn, Golden Cross	0	0	0	0	0	1	0	1	1	0	2	3
Bromegrass, Sac Smooth	0	0	0	0	0	0	0	0	1	0	1	1
Oats, Clintland 64	0	1	1	1	2	3	1	4	5	3	7	9
Radish, Cherry Belle	0	1	1	1	2	3	2	6	6	5	11	12
Periwinkle, Bright Eyes	0	0	0	0	0	0	0	0	0	0	0	0
Wheat, Wells	0	0	0	0	0	0	0	0	0	0	0	0
Squash, Summer	0	0	0	0	0	0	0	0	0	0	0	0

[a] The concentrations given in the column headings were divided by 1.4 in order to convert them into values equivalent to those used in generating the foliar injury equations for these cultivars.[17]

APPENDIX A

Annual Second-Highest Ozone Concentrations versus Averaging Times for Twenty-four Site-Years of Data[90]

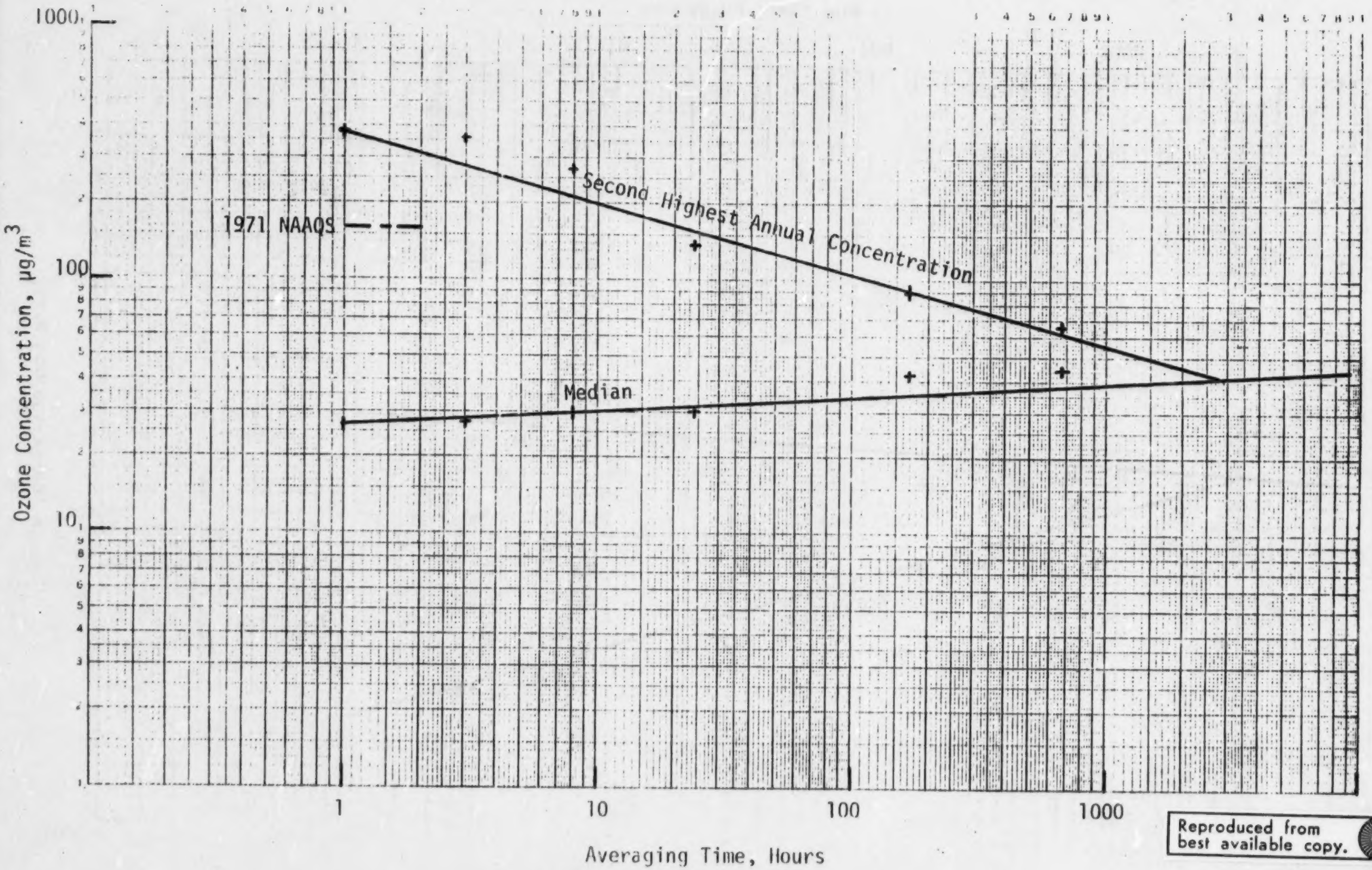

Figure A-1 Camden, NJ, 1973 (68 percent data)

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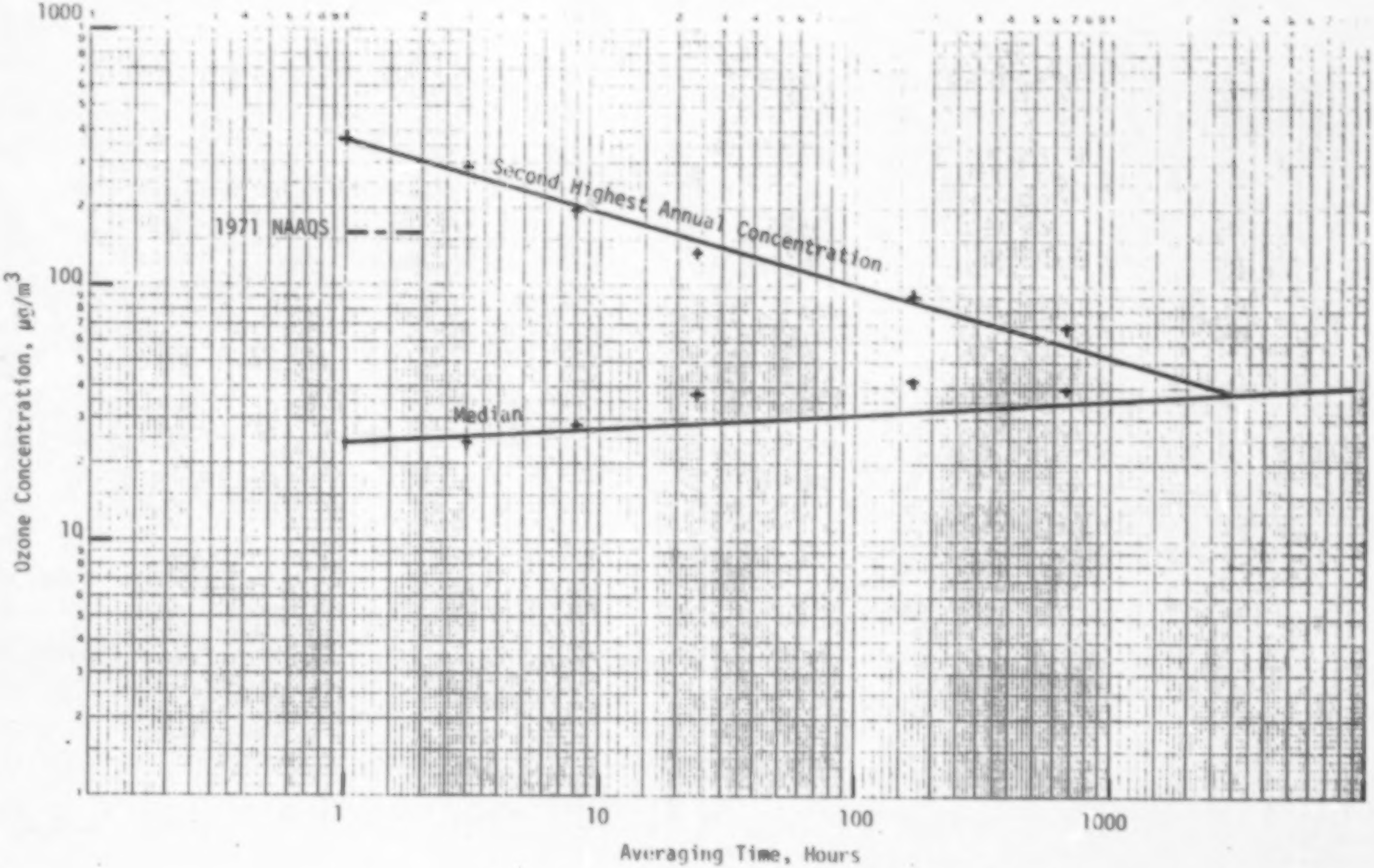

Figure A-2 Camden, NJ, 1974 (90 percent data)

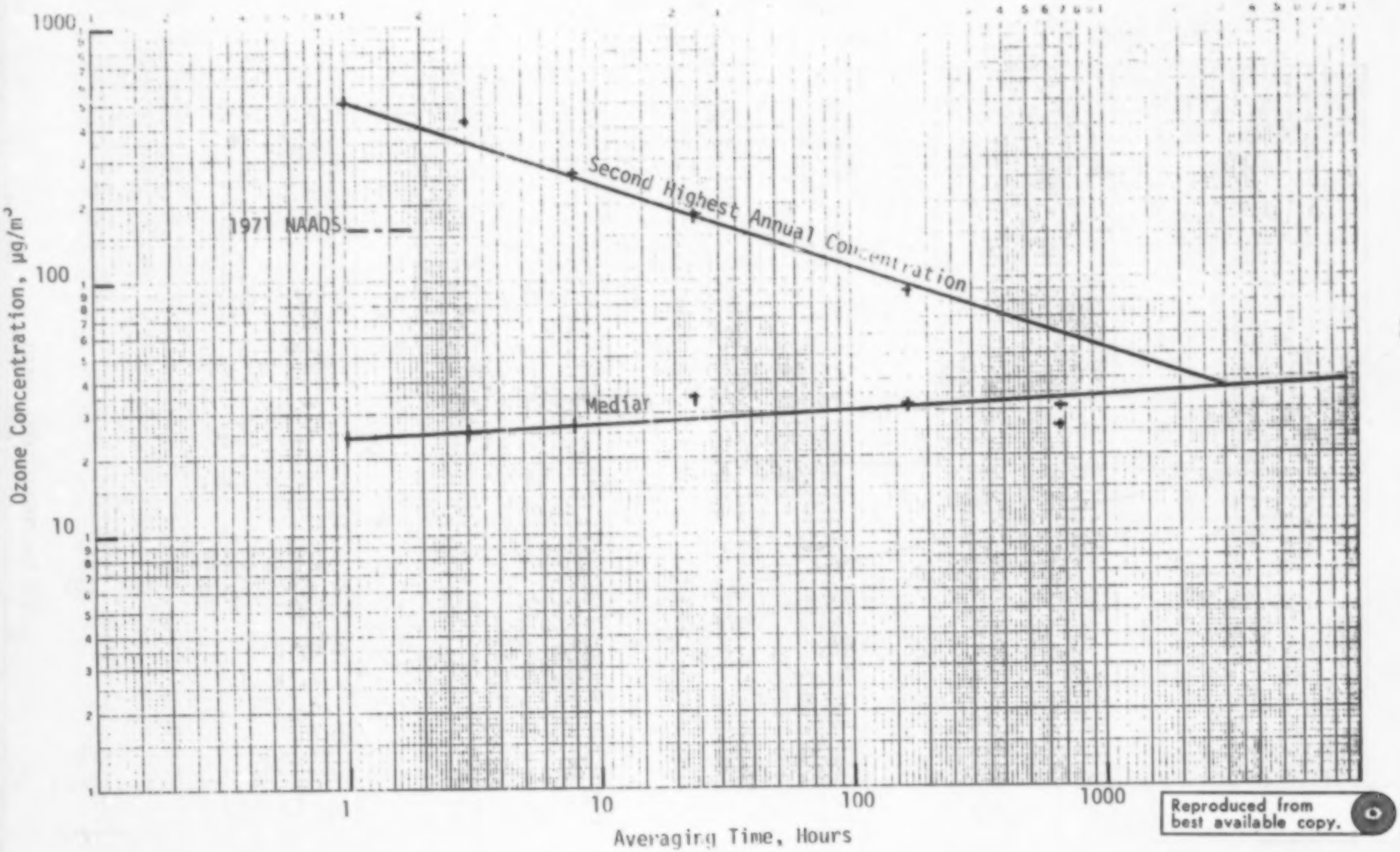

Figure A-3 Camden, NJ, 1975 (63 percent data)

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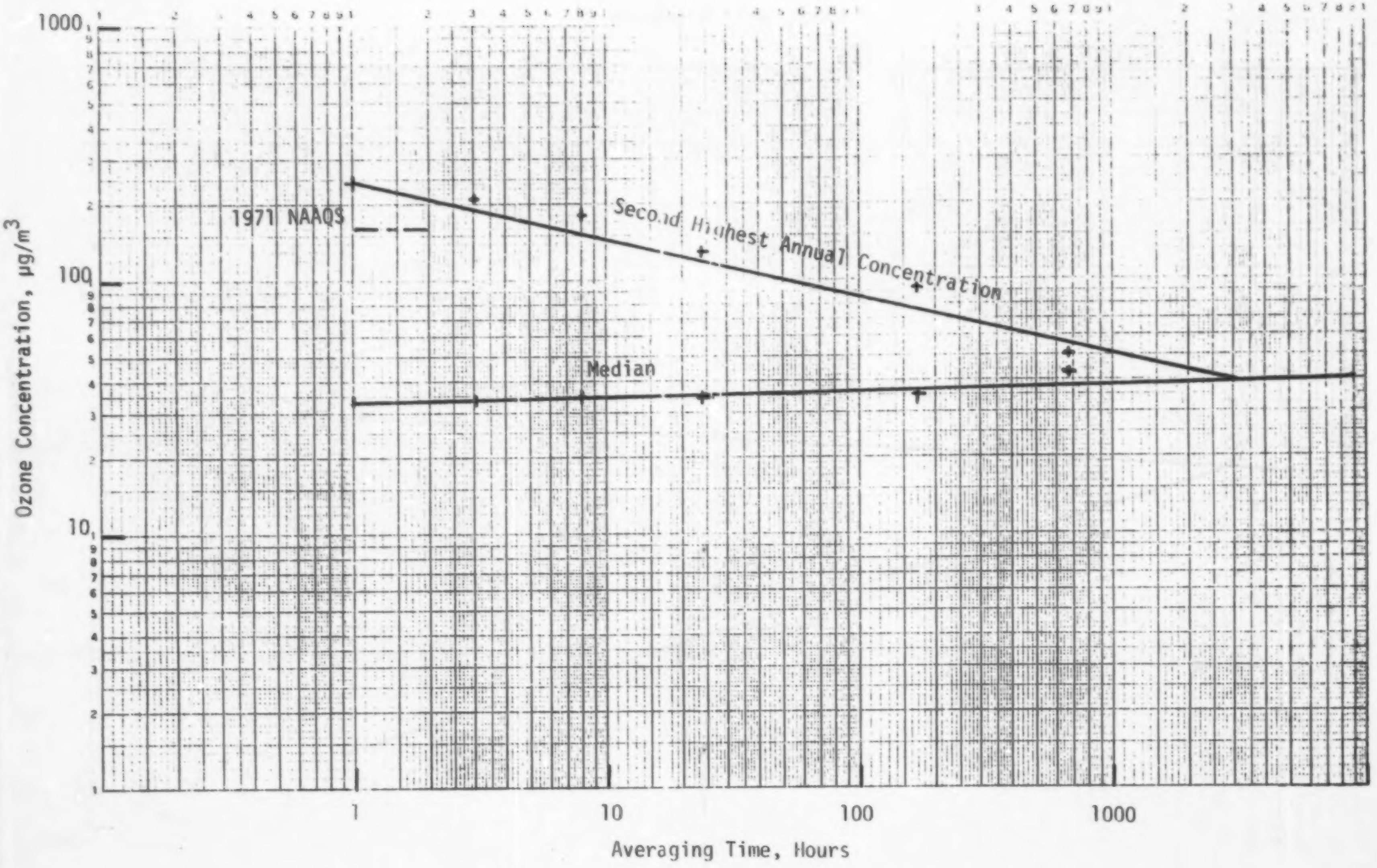

Figure A-4 Corpus Christi, TX, 1974 (80 percent data)

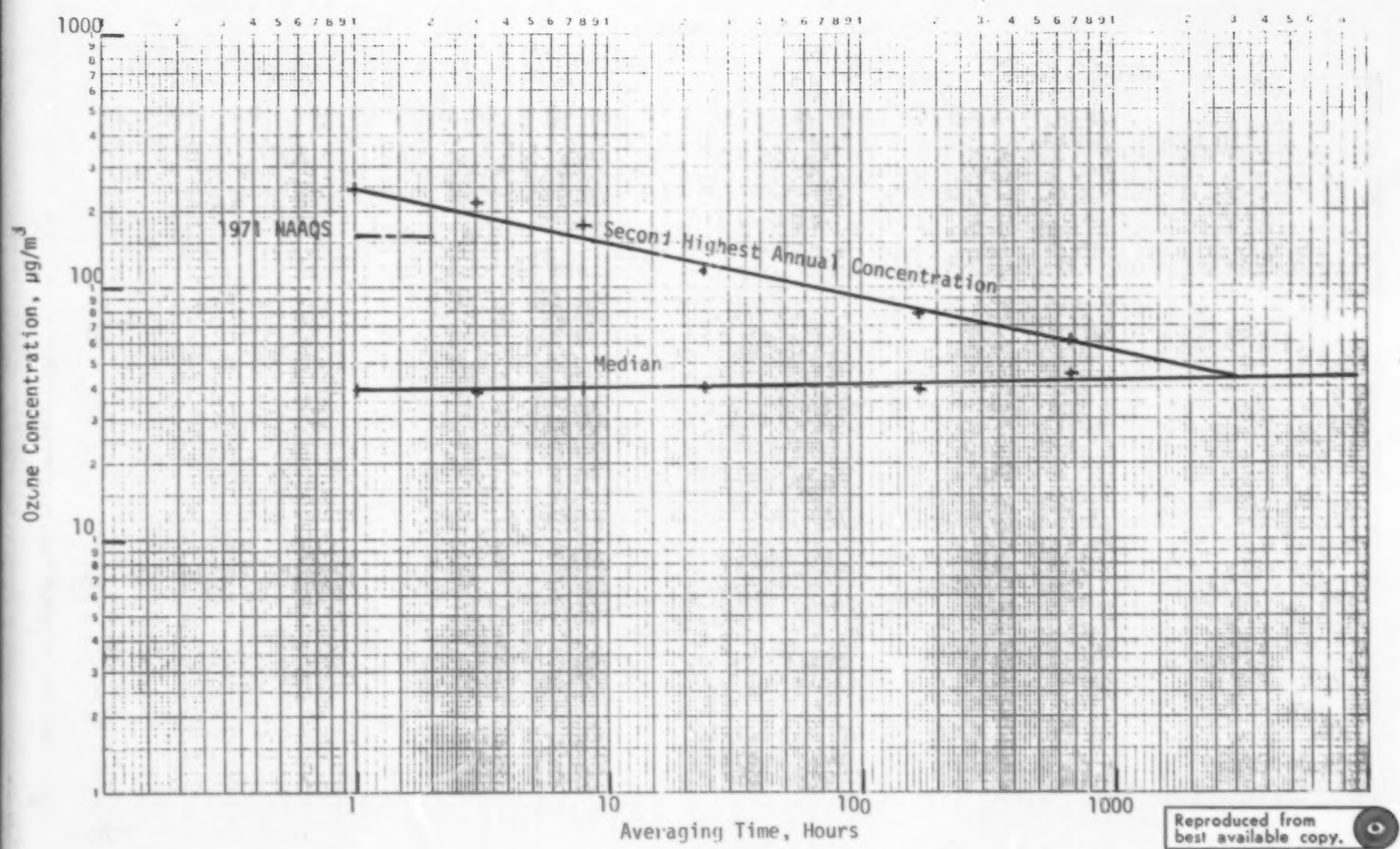

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Figure A-5 Corpus Christi, TX, 1975 (70 percent data)

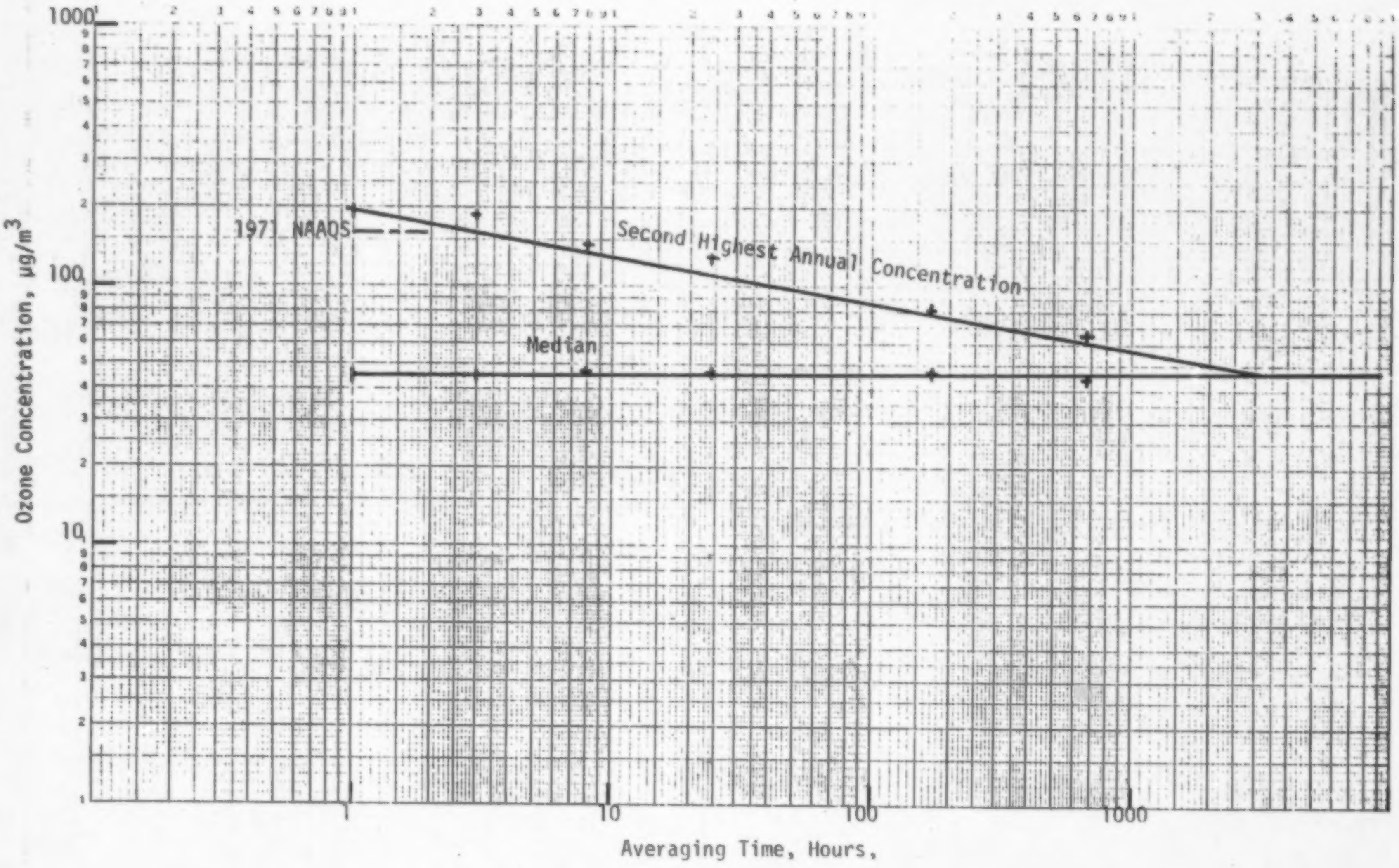

Figure A-6 Des Moines, IA, 1975 (90 percent data)

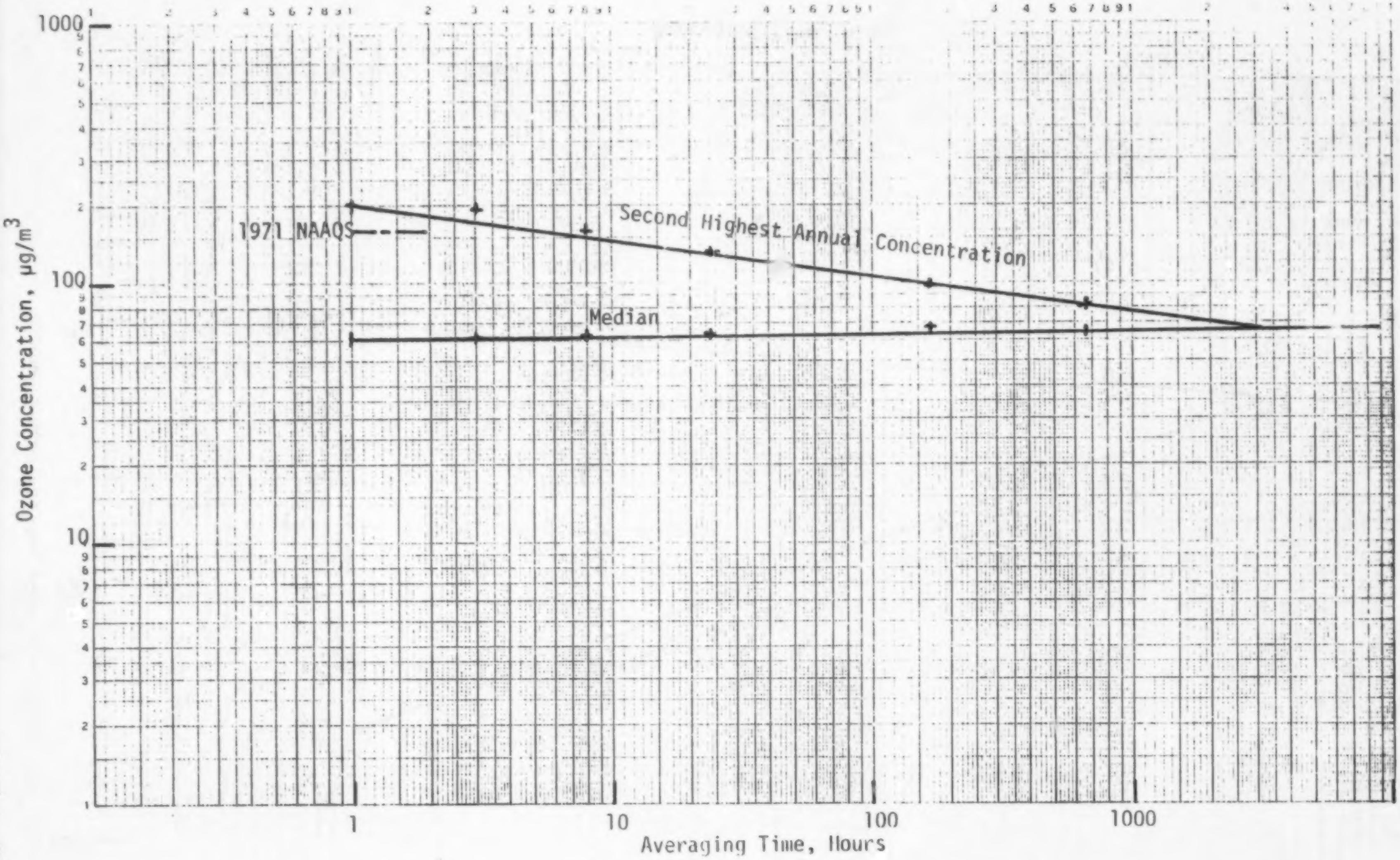

Figure A-7 Des Moines, IA, 1976 (72 percent data)

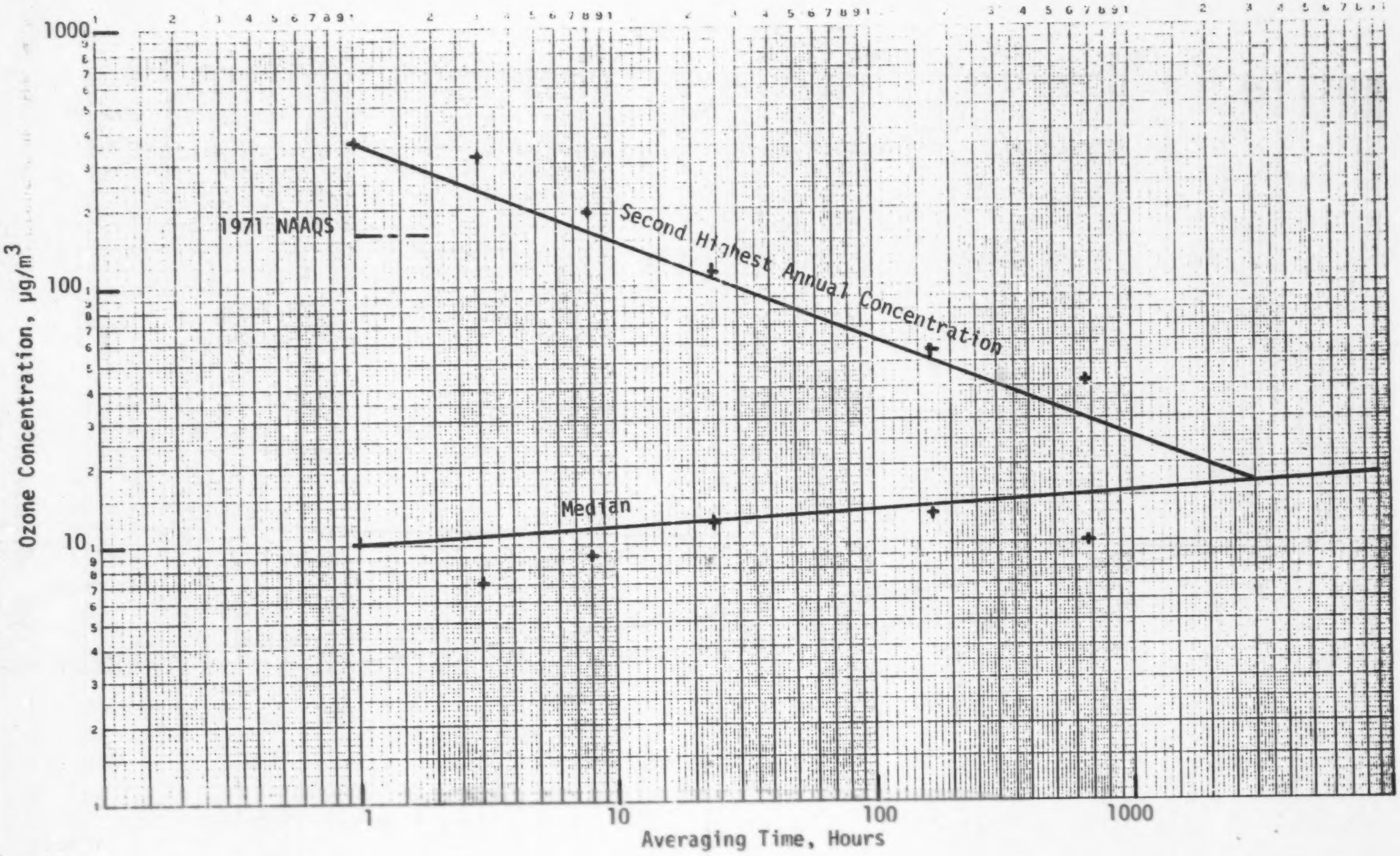

Figure A-8 Louisville, KY, 1973 (89 percent data)

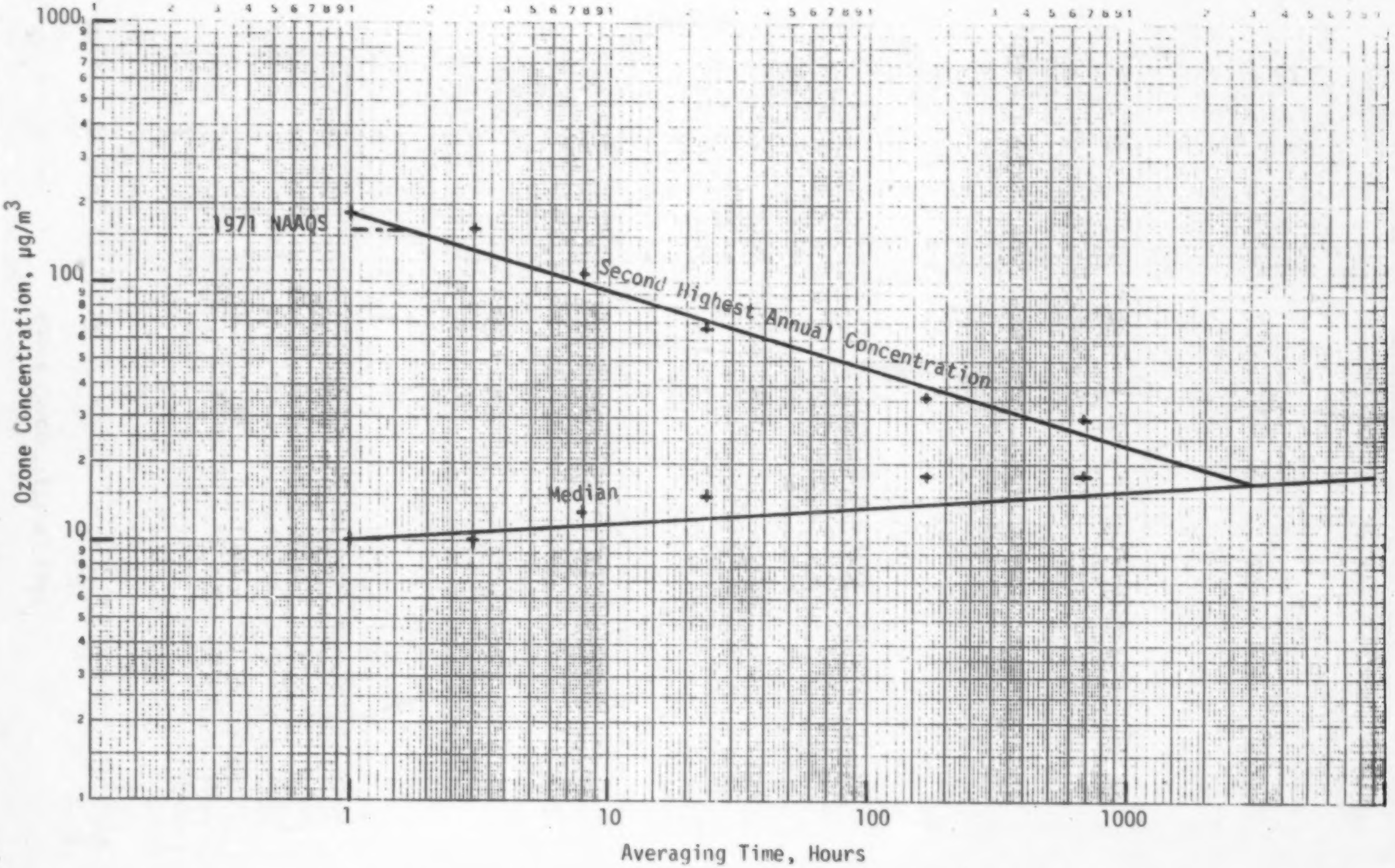

Figure A-9 Louisville, KY, 1974 (97 percent data)

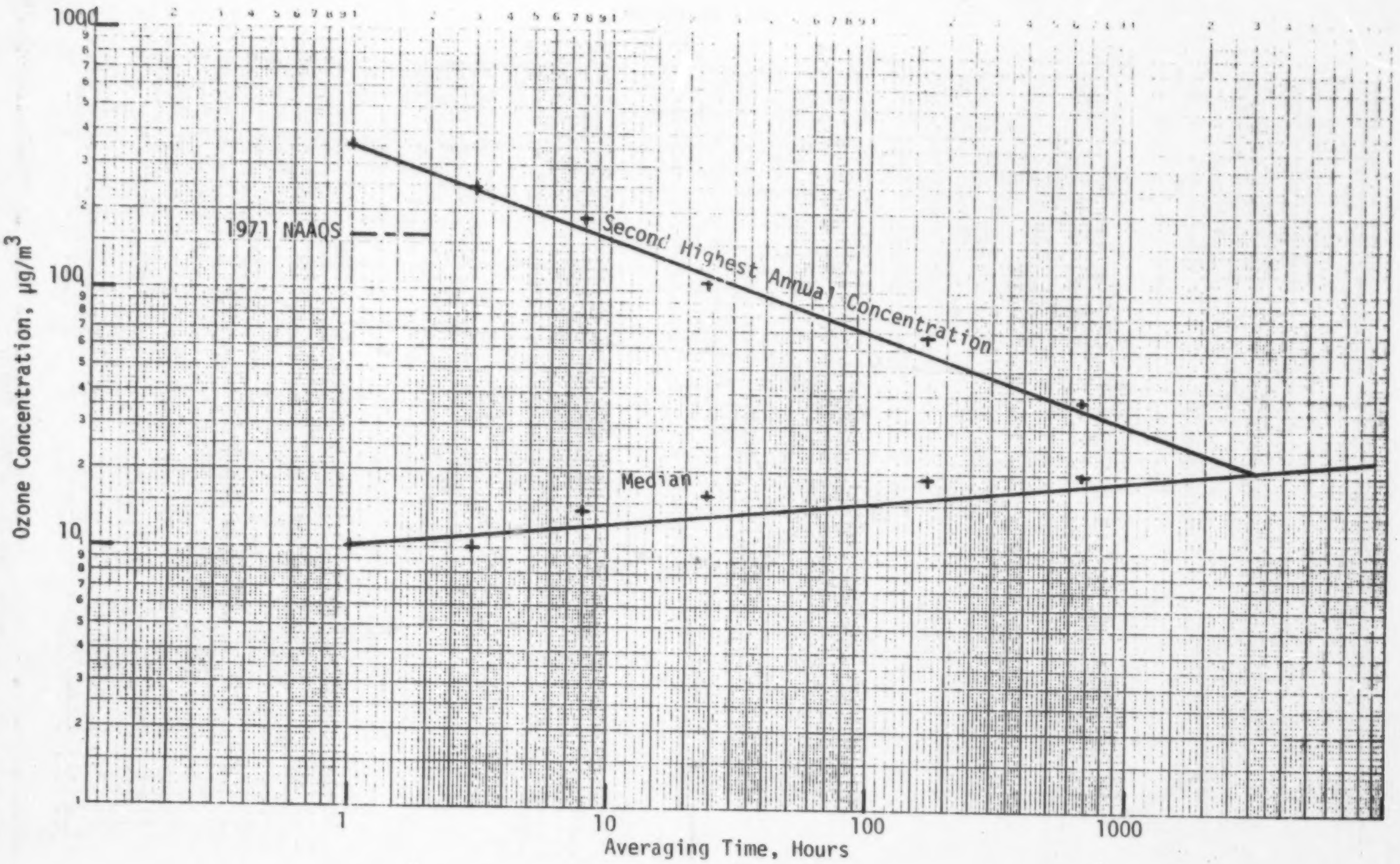

Figure A-10 Louisville, KY, 1975 (99 percent data)

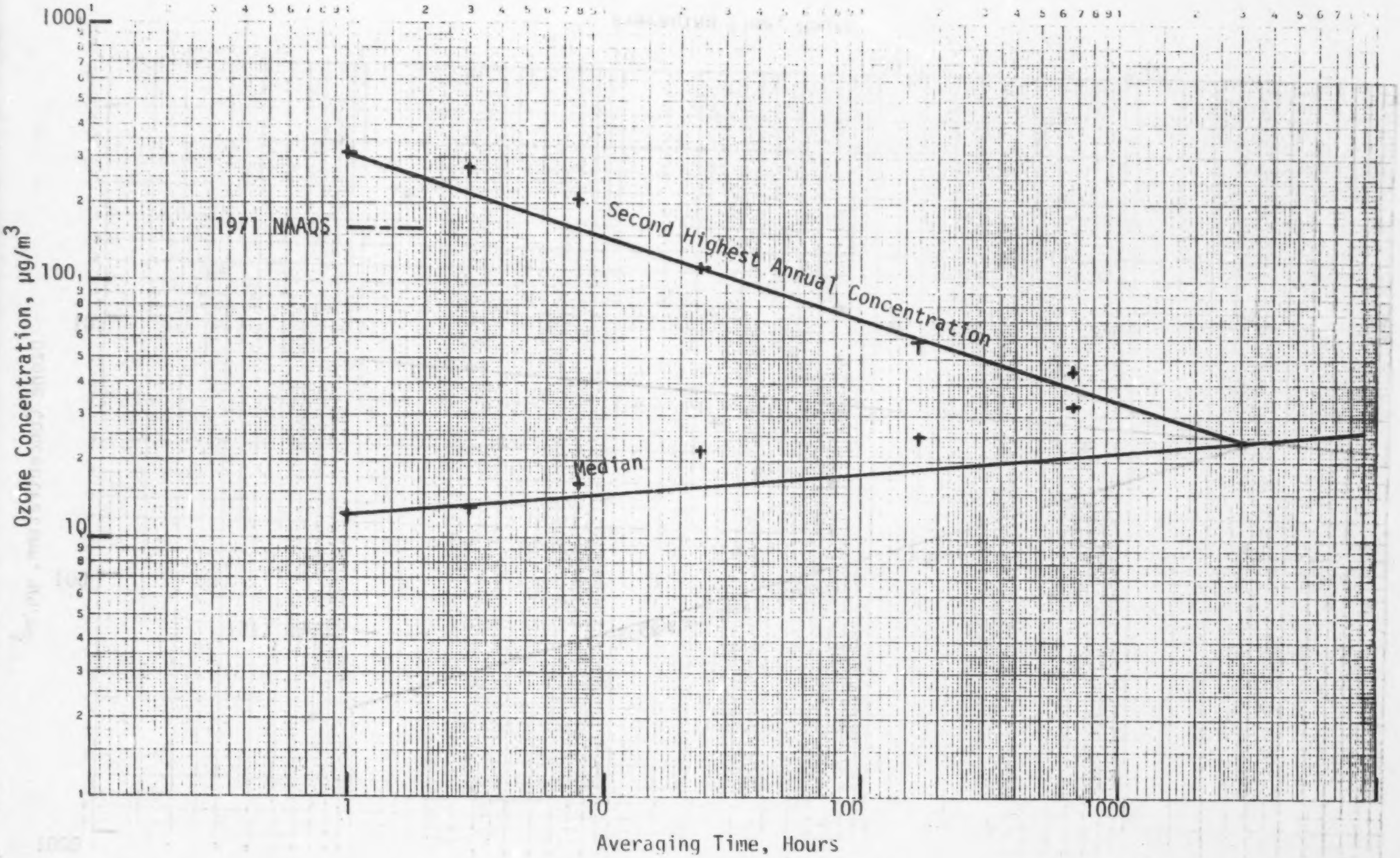

Figure A-11 Mamaroneck, NY, 1973 (64 percent data)

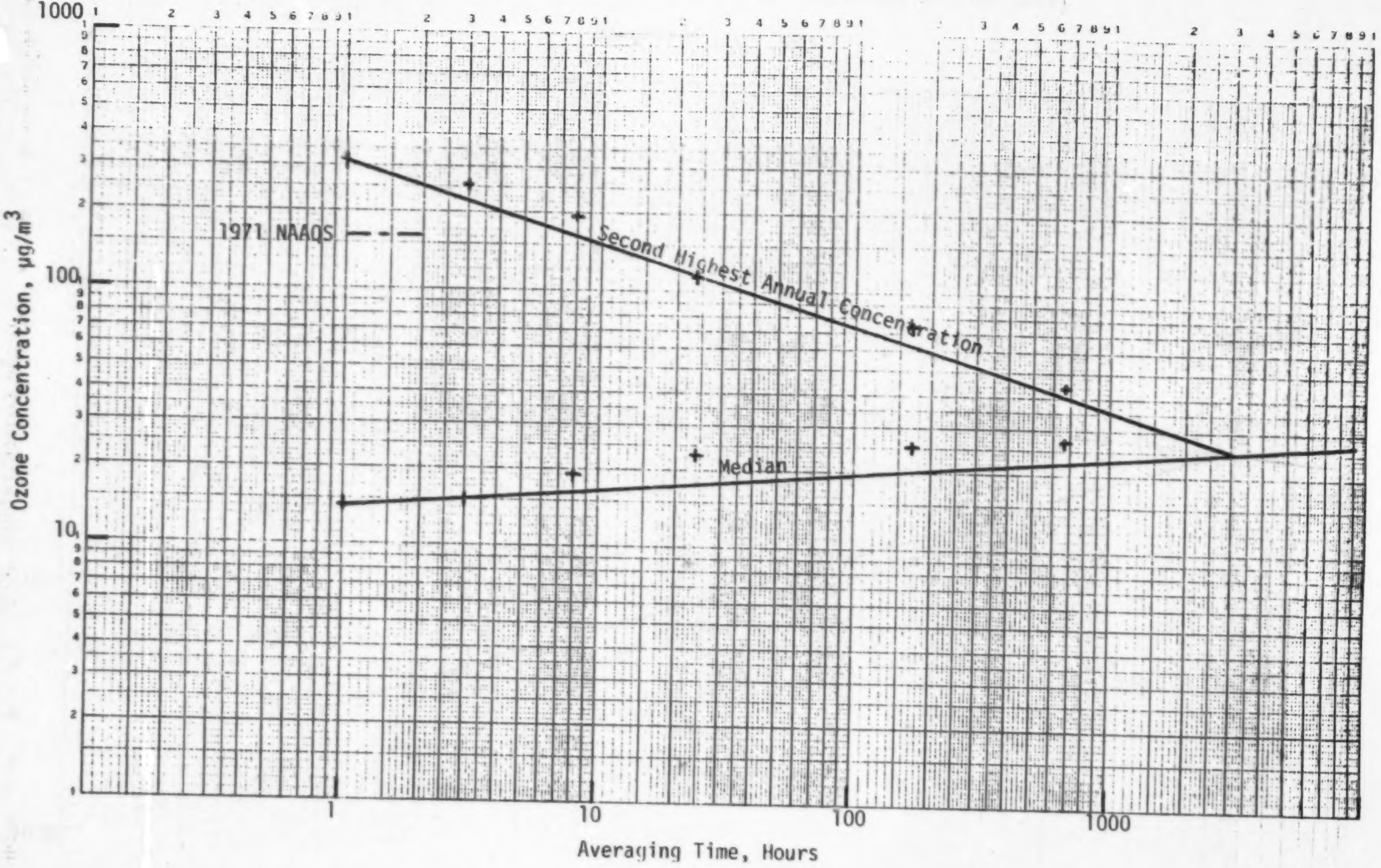

Figure A-12 Mamaroneck, NY, 1974 (94 percent data)

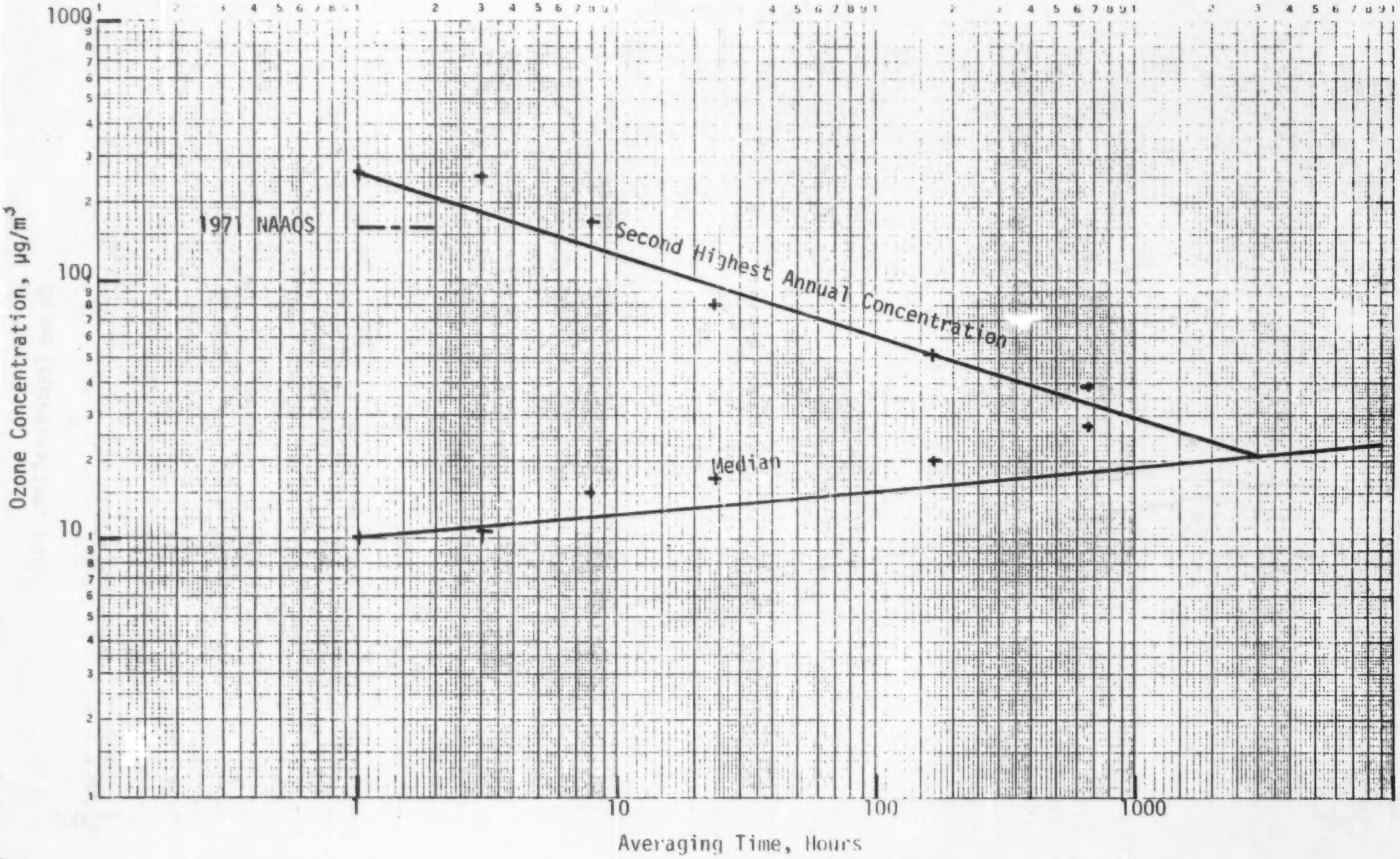

Figure A-13 Mamaroneck, NY, 1975 (84 percent data)

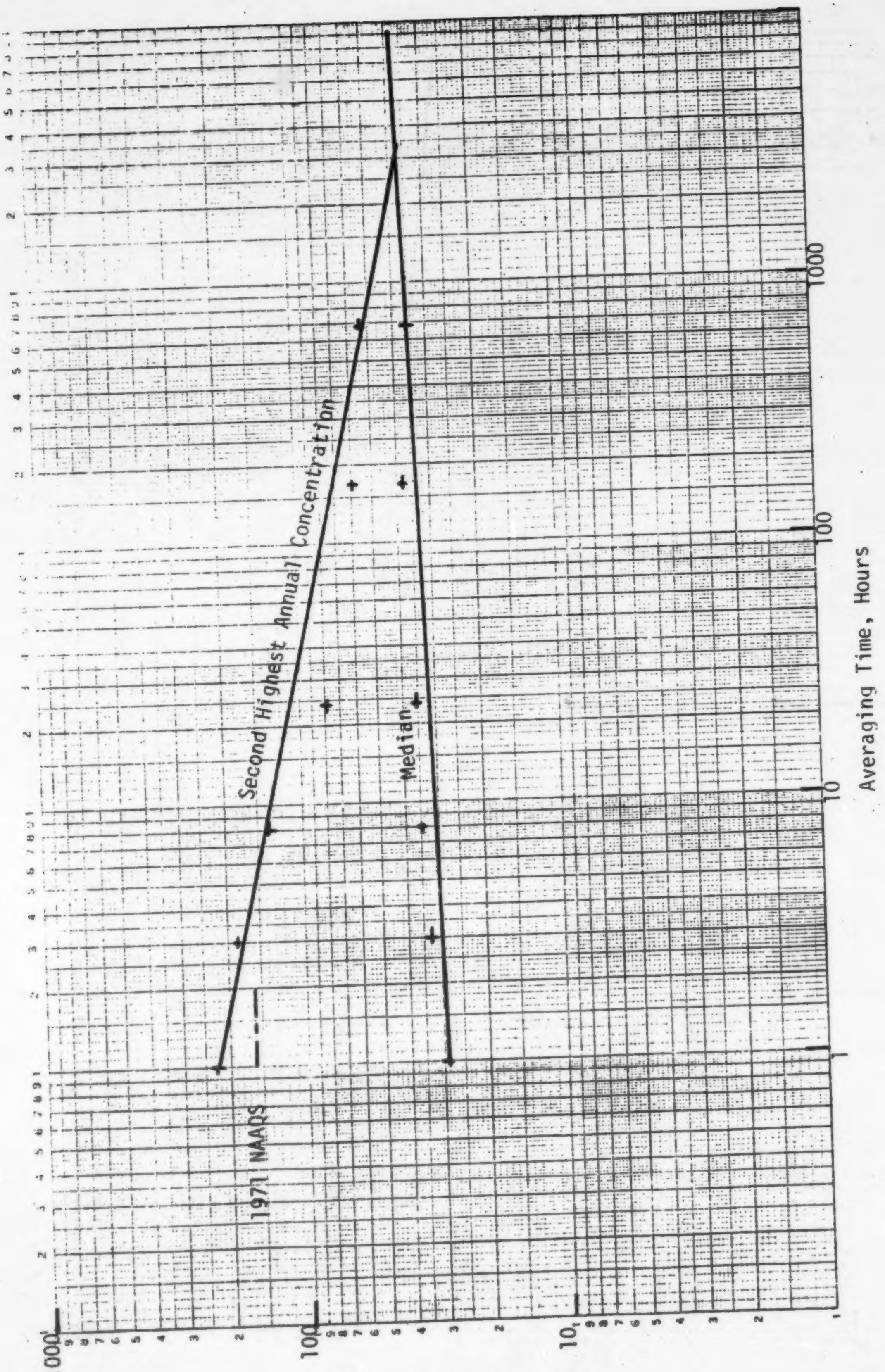

Figure A-14 Memphis, TN, 1974 (95 percent data)

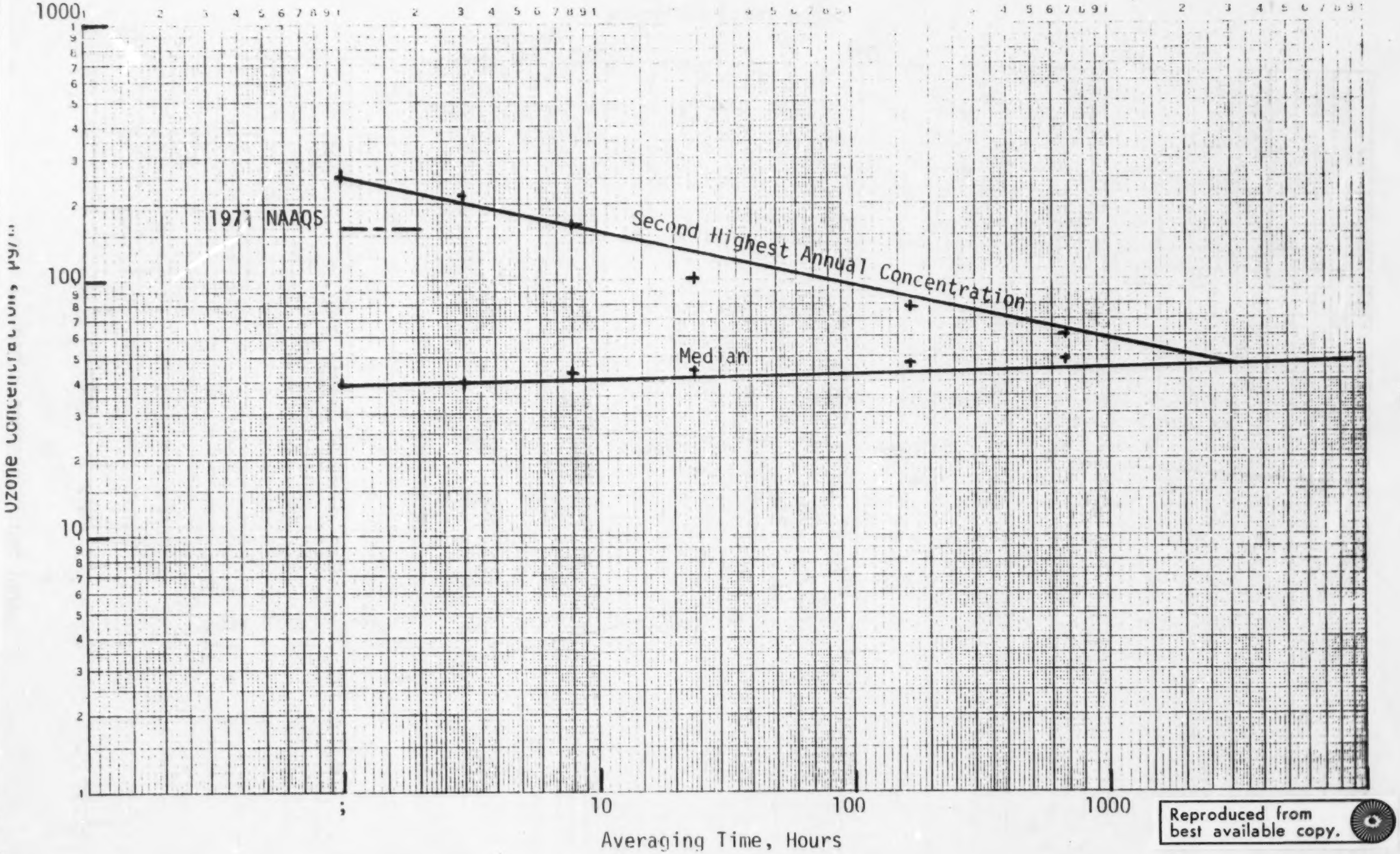

Figure A-15 Memphis, TN, 1975 (91 percent data)

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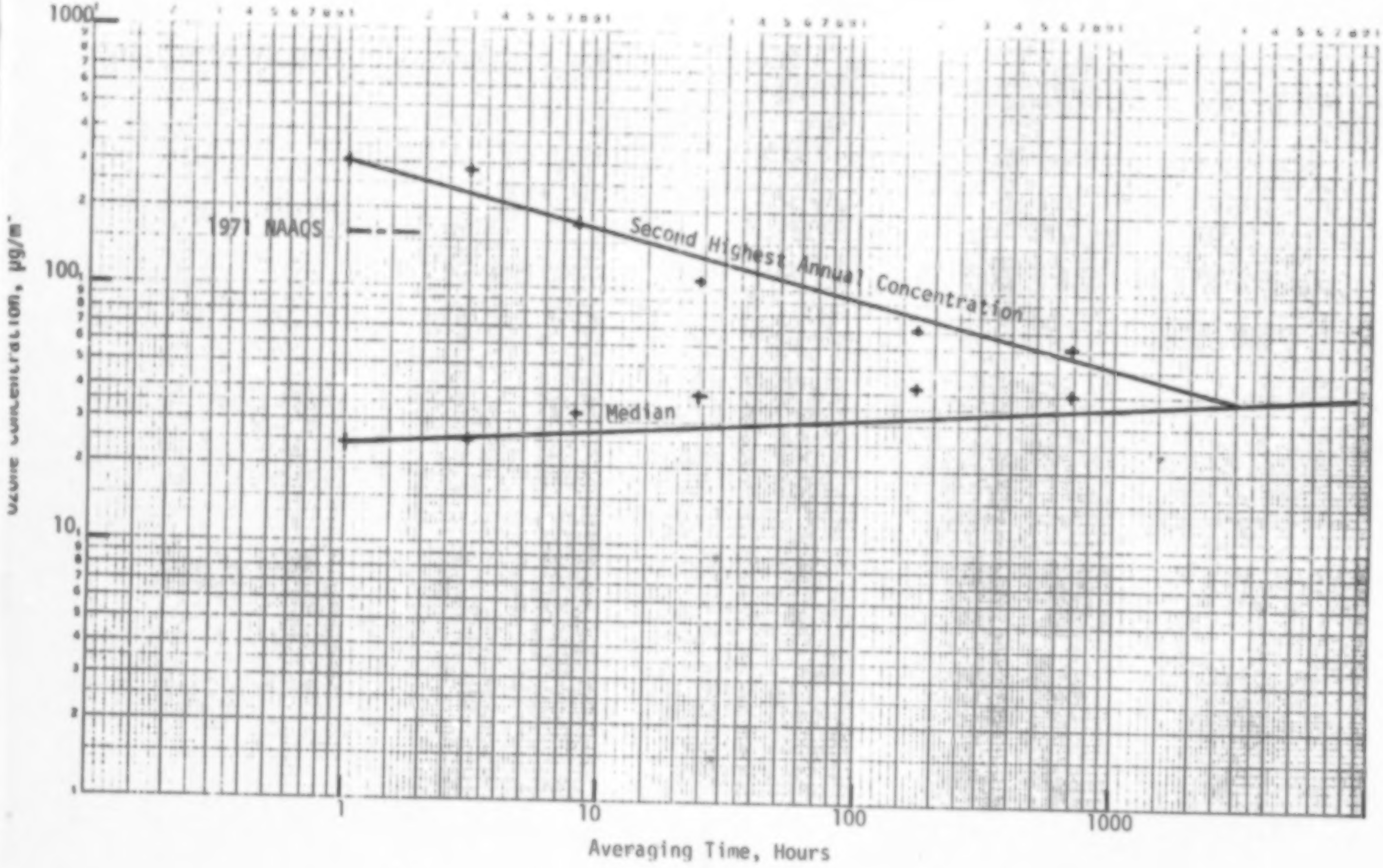

Figure A-16 Newport, KY, 1973 (77 percent data)

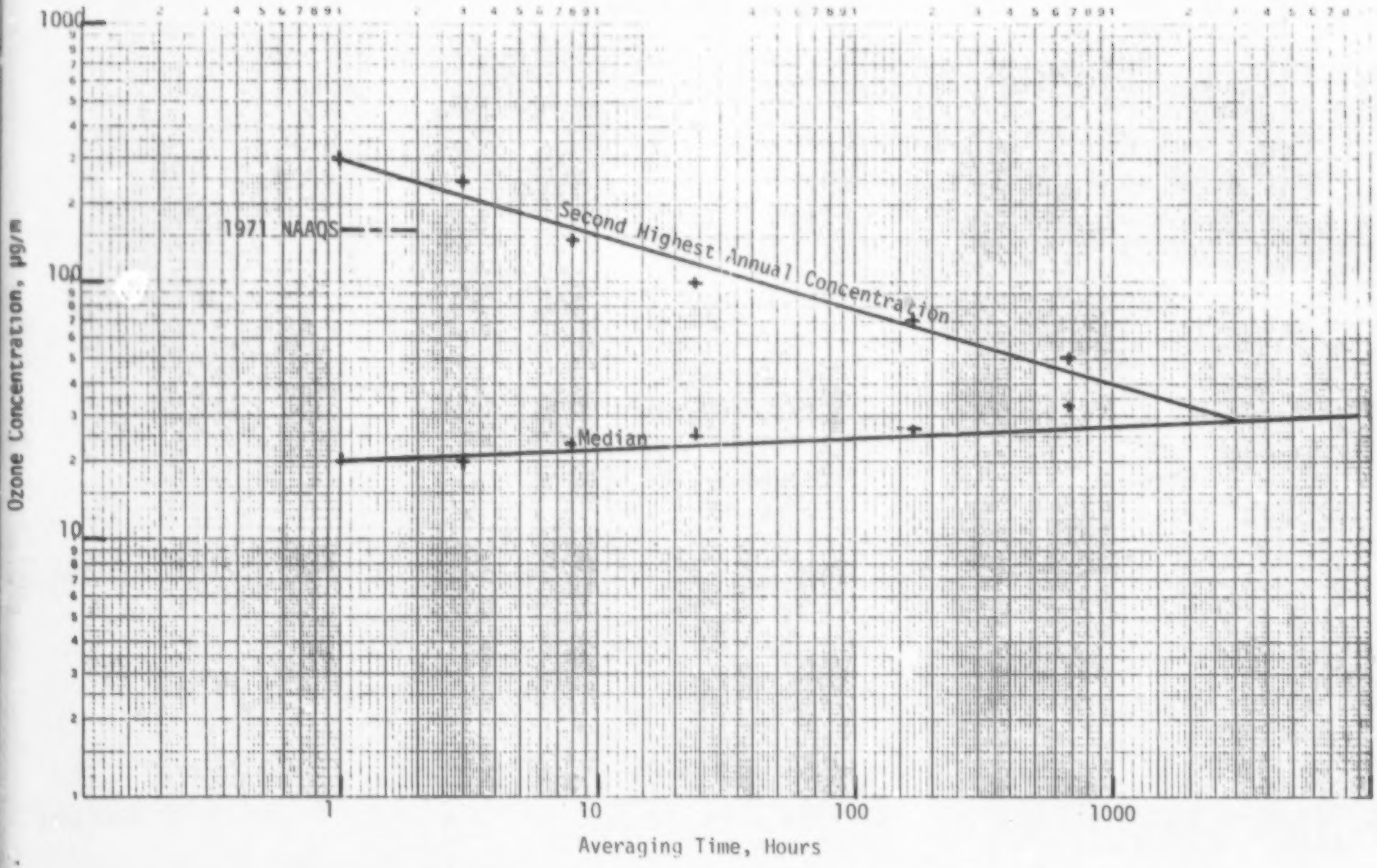

Figure A-17 Newport, KY, 1974 (95 percent data)

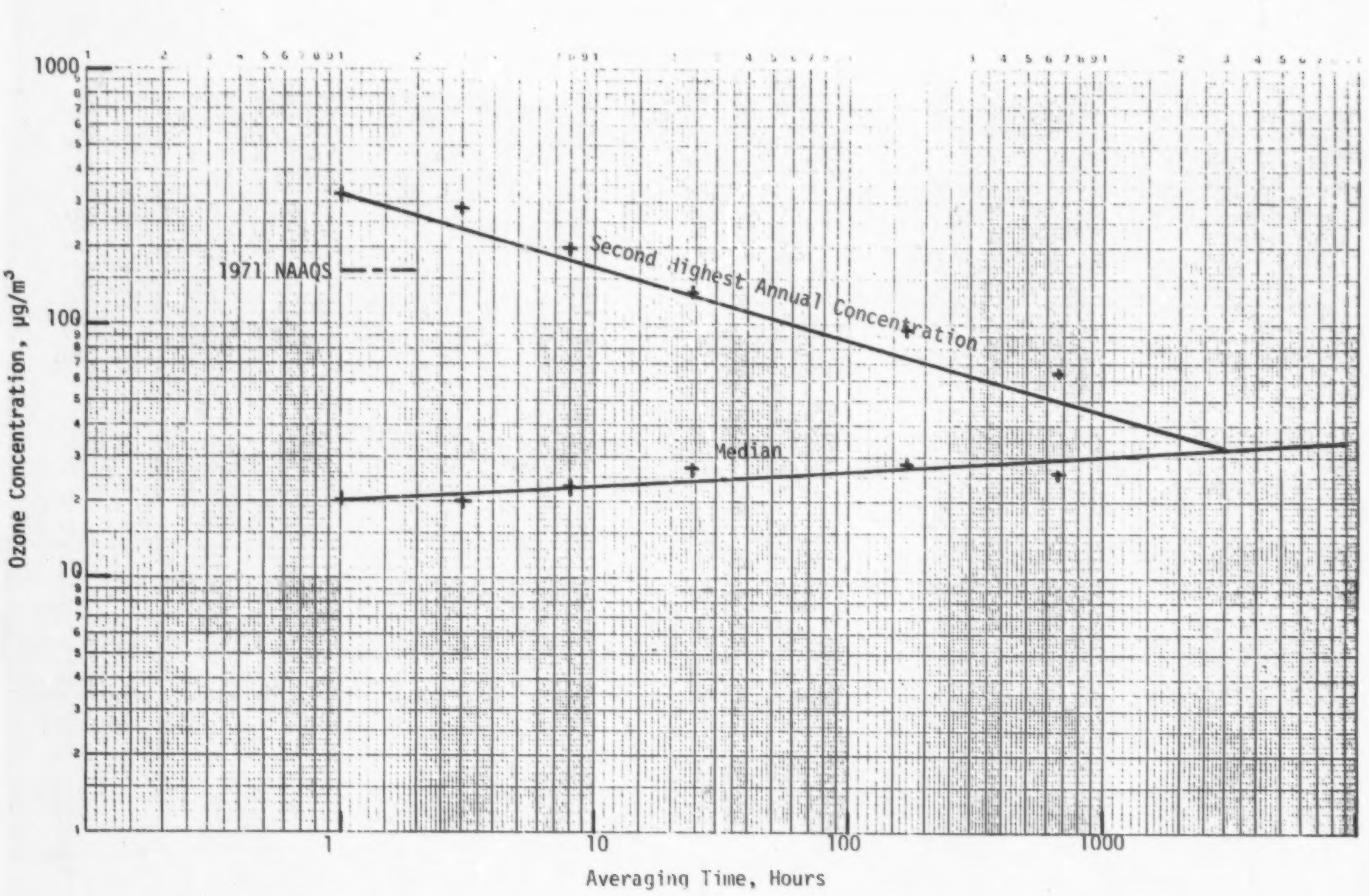

Figure A-18 Newport, KY, 1975 (92 percent data)

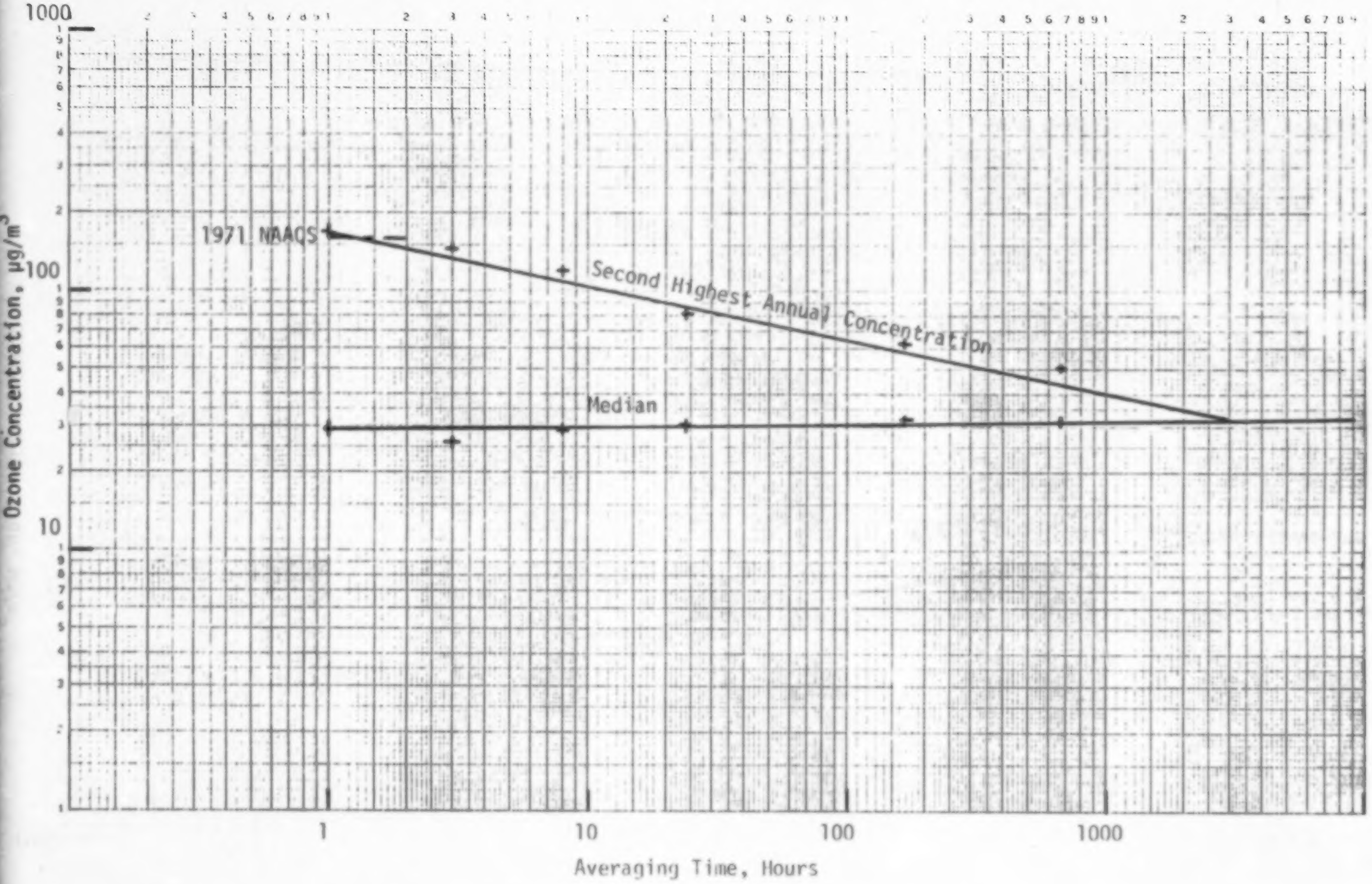

Figure A-19 Omaha, NE, 1974 (90 percent data)

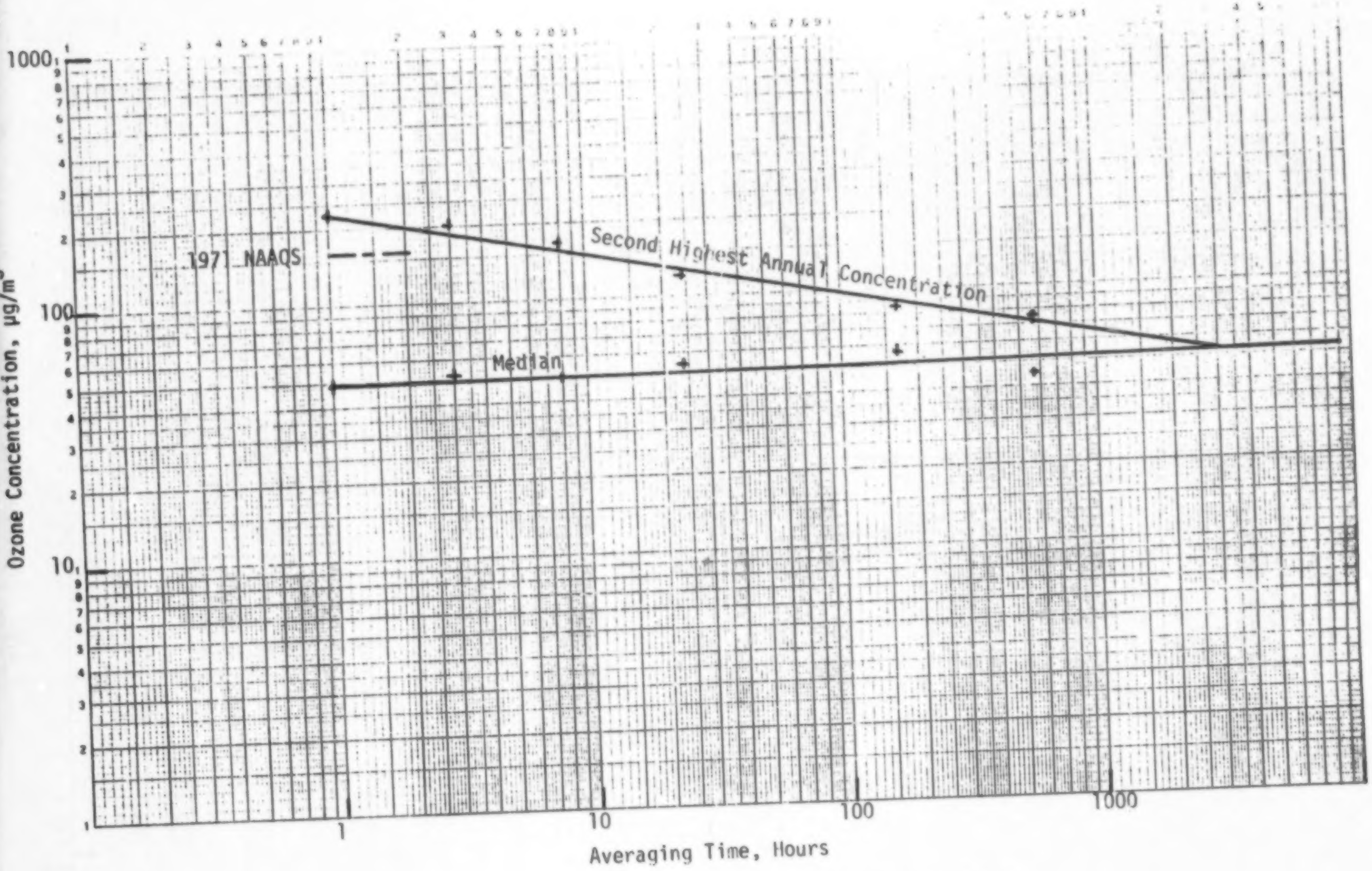

Figure A-20 Omaha, NE, 1975 (83 percent data)

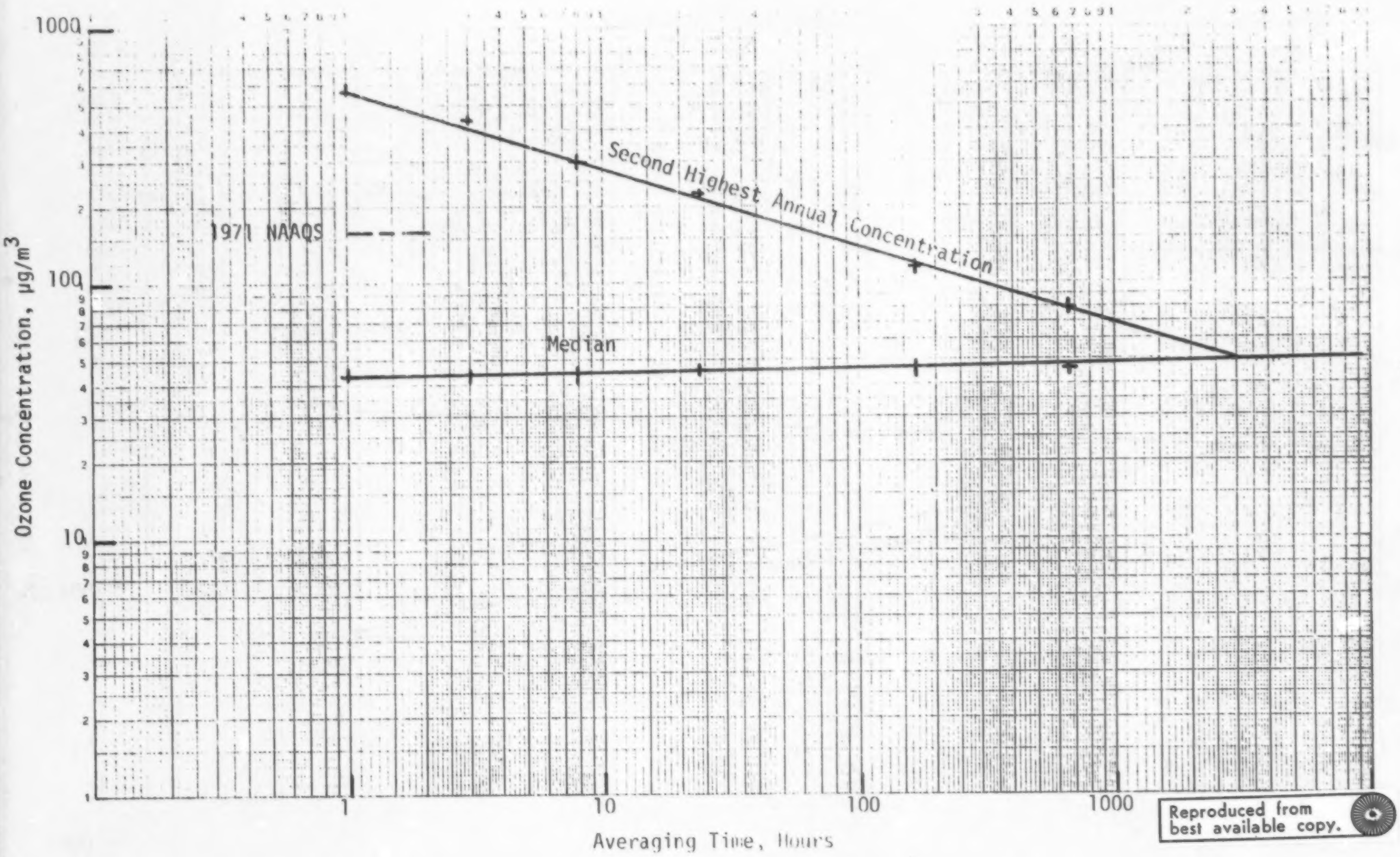

Figure A-21 Racine, WI, 1974 (95 percent data)

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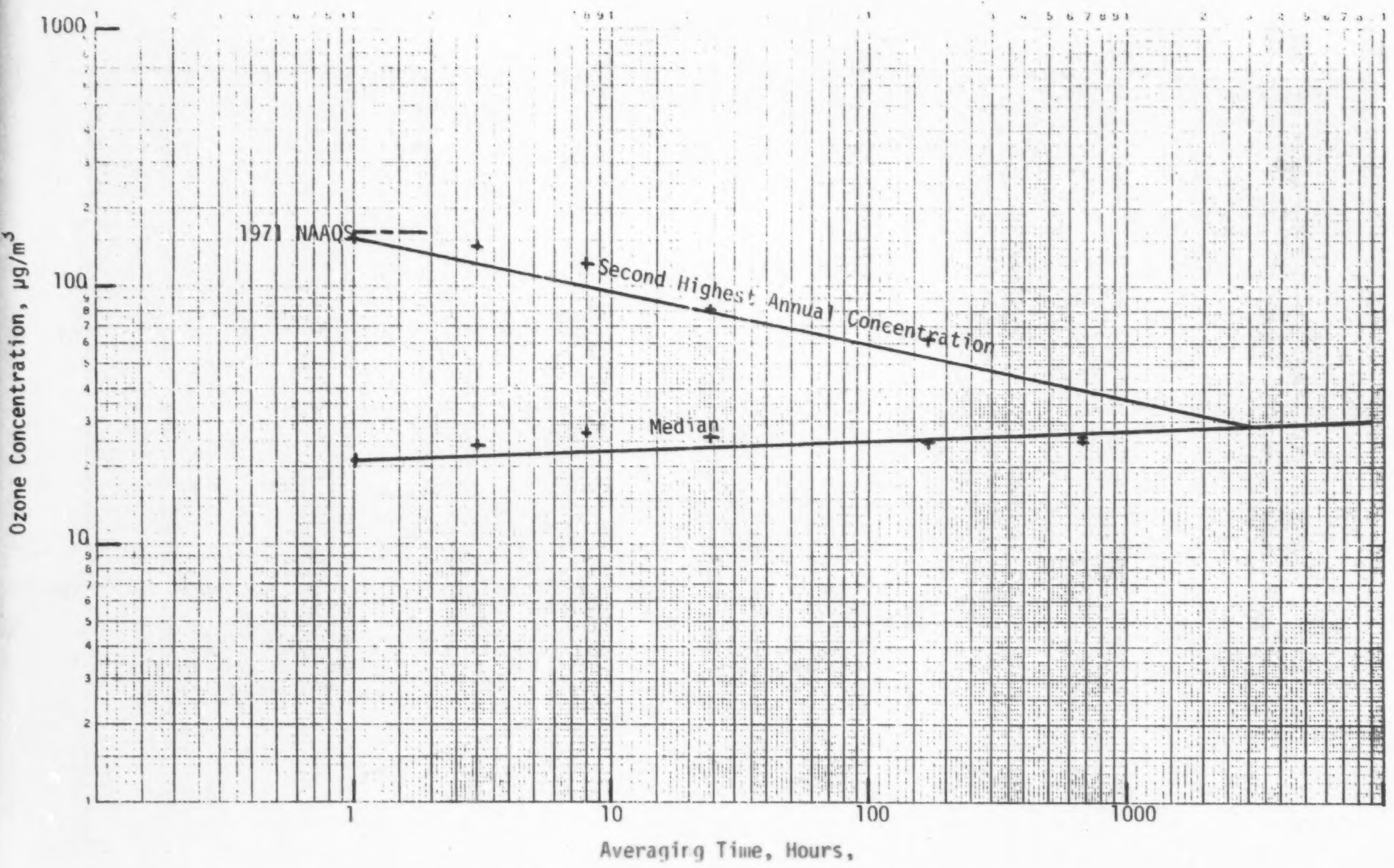

Figure A-22 Richland Co, SC, 1973 (65 percent data)

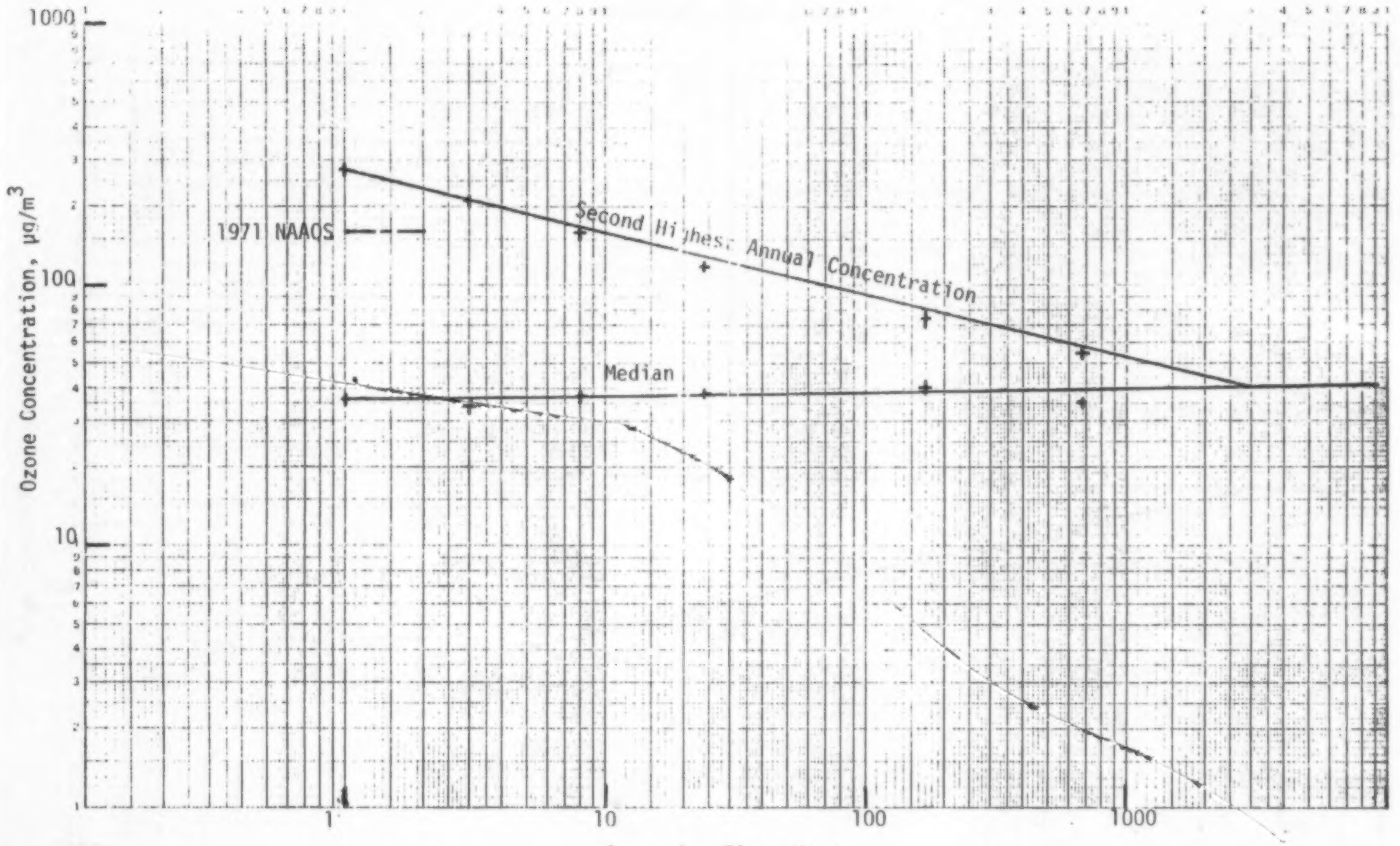

Figure A-23 Richland Co, SC, 1974 (94 percent data)

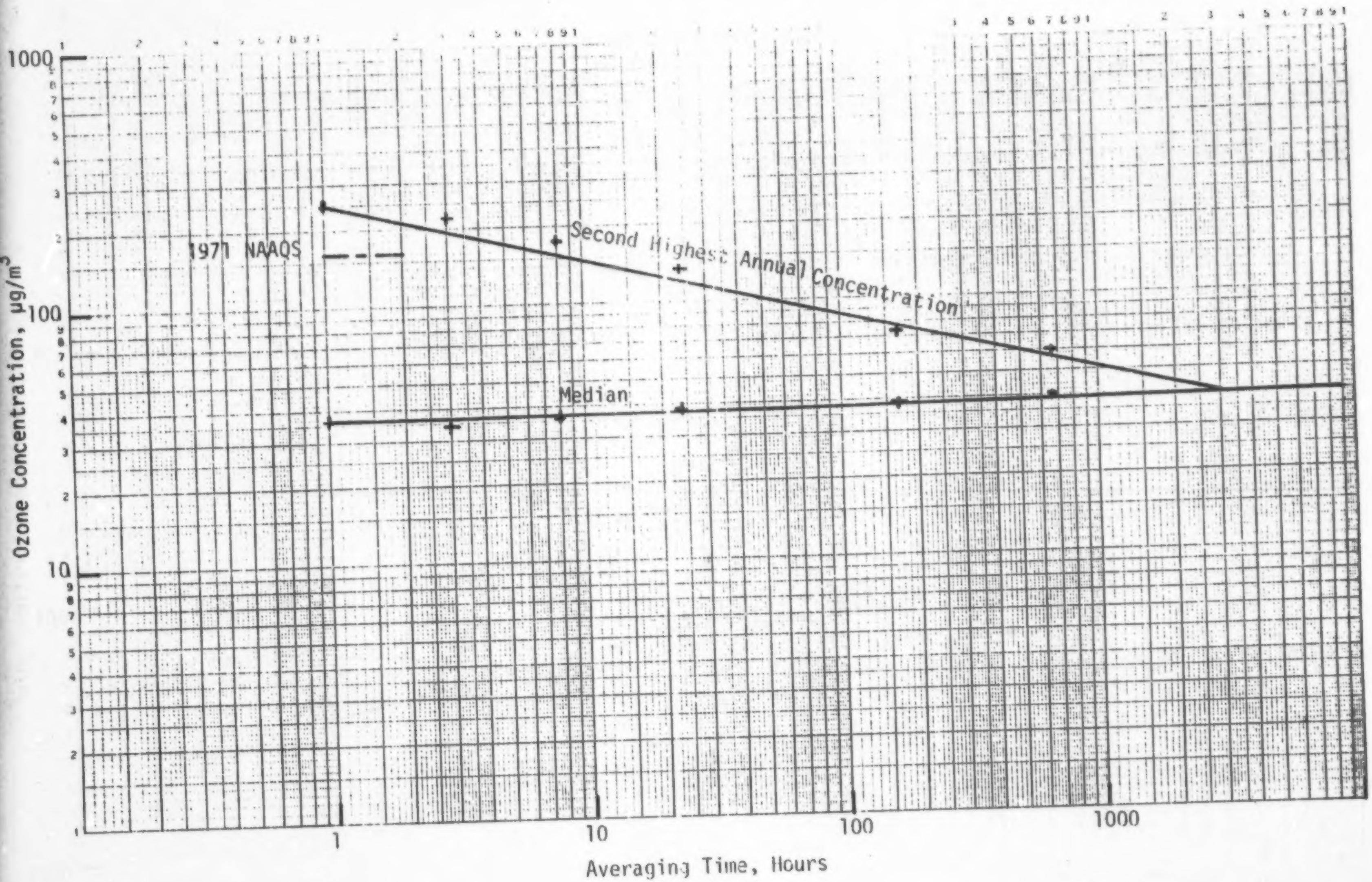

Figure A-24 Richland Co, SC, 1975 (98 percent data)

Appendix B

Calculation of Exposures Expected to Accompany Alternative Standard Levels

This appendix explains the computation for different short-term averaging times of the maximum exposure levels which are expected to accompany alternative hourly average standards, and estimates long-term exposure patterns expected to accompany such standards.

1. Weibull Frequency Distribution

For the purposes of this document, the Weibull frequency distribution was assumed to provide a reasonably good description of the frequencies at which ambient ozone concentrations occur in urban areas. This assumption was based on an analysis of ozone data collected during 22 site-years in 14 urban areas across the nation, as presented in a draft report[78] prepared for EPA by PEDCo Environmental, Inc. (referred to henceforth as the PEDCo report).

A useful form of the Weibull frequency distribution equation is:

$$G(x) = \exp -\left(\frac{x}{\delta}\right)^k \qquad \text{(B-1)}$$

where $G(x)$ is the fraction of the total members of a population having a value greater than x, and k and δ are two parameters of the frequency distribution. The Weibull distribution is readily adapted for analysis of an air quality standard expressed in a statistical form. Such a standard level, c_{std}, is expected to be exceeded no more than E times per year. If the standard level is based on an averaging time such that there can be a total of n measurements in a year, one has:

$$G(c_{std}) = \frac{E}{n} = \exp -\left[\frac{c_{std}}{\delta}\right]^k \qquad \text{(B-2)}$$

Rearranging this equation enables one to define the parameter δ in terms of the standard specifications, like so:

$$\delta = \frac{c_{std}}{\left[\ln \frac{n}{E}\right]^{1/k}} \qquad \text{(B-3)}$$

There will be different frequency distributions for different averaging times, and the parameters for these are designated in this appendix by subscripts, e.g., k_{1hr} and δ_{3hr}.

2. Short-term Exposure Levels

This section will for illustrative purposes examine an hourly average standard of 0.08 ppm (157 $\mu g/m^3$) for which E equals one in order to evaluate the 3- and 8-hour-average concentrations (designated as c^*_{3hr} and c^*_{8hr}, respectively) which may be expected to be exceeded only once per year.

To begin this analysis, one must choose a value of the parameter k_{1hr} suitable for an area attaining a 0.08 ppm hourly average standard level. The average k_{1hr} for the 22 urban site-years listed in Table 5-1 of the PEDCo report is 1.05. None of these sites attained the current standard; several had more than 200 hours above 160 $\mu g/m^3$ (as indicated in Table 6-1 of the PEDCo report). However, an examination of those sites with relatively few hours (less than 60) above the standard level along with other data from two site-years at Kansas City, Kansas which did attain the standard indicates that a k_{1hr} value of about 1.25 provides a reasonably good estimate of what might be expected for an average k_{1hr} value in urban areas attaining a 0.08 ppm hourly average standard.

Having selected an average k_{1hr}, one can use equations B-4 and B-5 (which were obtained by linear regression analyses of the k values in Table 5-1 of the PEDCo report) to determine k_{3hr} and k_{8hr}. It is assumed that the relationship between the k parameters for different averaging times which is indicated by Table 5-1 is valid when a 0.08 ppm standard level is attained.

$$k_{3hr} = 1.02\ k_{1hr} + 0.014 = 1.289 \qquad \text{(B-4)}$$

$$k_{8hr} = 1.23\ k_{1hr} - 0.043 = 1.495 \qquad \text{(B-5)}$$

The correlation coefficients (R^2) for equations B-4 and B-5 are 0.98 and 0.92, respectively, indicating a reasonably good fit with the data.

Using the selected k_{1hr}, one can determine δ_{1hr} from equation B-3:

$$\delta_{1hr} = \frac{c_{std}}{\left[\ln \frac{n}{E}\right]^{1/k_{1hr}}} = \frac{157\ \mu g/m^3}{\left[\ln \frac{8760}{1.0}\right]^{1/1.25}} = 26.9\ \mu g/m^3 \qquad \text{(B-6)}$$

For given δ_{1hr} and k_{1hr}, Figure 2-1 in the PEDCo report permits calculation of the annual average concentration, $\overline{x}$, as follows:

$$\text{For } k_{1hr} = 1.25,\ \frac{\overline{x}}{\delta_{1hr}} = 0.938, \text{ so } \overline{x} = 25.2\ \mu g/m^3 \qquad \text{(B-7)}$$

The annual average concentration $\overline{x}$ is the same regardless of whether data expressed in 1-, 3-, or 8-hour averaging times are used to compute $\overline{x}$. This fact enables one to calculate δ_{3hr} and δ_{8hr} using Figure 2-1:

$$\text{For } k_{3hr} = 1.289,\ \frac{\overline{x}}{\delta_{3hr}} = 0.931, \text{ so } \delta_{3hr} = 27.1\ \mu g/m^3 \qquad \text{(B-8)}$$

$$\text{For } k_{8hr} = 1.495,\ \frac{\overline{x}}{\delta_{8hr}} = 0.903, \text{ so } \delta_{8hr} = 27.9\ \mu g/m^3 \qquad \text{(B-9)}$$

Finally, one may determine the concentration c which is expected to be exceeded E times per year for 3-hour or 8-hour averaging times by returning to the Weibull frequency distribution equation:

$$G(c) = \frac{E}{n} = \exp -\left(\frac{c}{\delta}\right)^{k} \qquad \text{(B-1)}$$

Rearranging the above equation yields

$$c = \delta \left(\ln \frac{n}{E}\right)^{1/k} \qquad \text{(B-10)}$$

Thus,

$$c^{*}_{3hr} = \delta_{3hr} \left[\ln \frac{2920}{1.0}\right]^{1/k_{3hr}} = 136\ \mu g/m^3\ (0.069\ ppm) \qquad \text{(B-11)}$$

$$c^{*}_{8hr} = \delta_{8hr} \left[\ln \frac{1095}{1.0}\right]^{1/k_{8hr}} = 103\ \mu g/m^3\ (0.052\ ppm) \qquad \text{(B-12)}$$

These are the concentrations expected to be exceeded only once per year for each averaging time in an urban area just attaining a 0.08 ppm hourly average standard level. These values are presented in the table below, along with corresponding values derived for alternative standard levels.

Table B-1

Short-Term Ozone Exposures Expected to Accompany Alternative Standard Levels

c_{std}, ppm ($\mu g/m^3$)	c^{*}, concentration expected to be exceeded only once per year for given averaging times, ppm ($\mu g/m^3$)		
	1 hour	3 hour	8 hour
0.06 (118)	0.060 (118)	0.052 (102)	0.039 (77)
0.08 (157)	0.080 (157)	0.069 (136)	0.052 (103)
0.10 (196)	0.100 (196)	0.086 (169)	0.065 (128)
0.12 (235)	0.120 (235)	0.104 (203)	0.078 (154)

Excerpts from this table are presented as column headings in Table 10 for use in the foliar injury analysis.

3. Long-term Exposure Patterns

The preceding computational technique may be used to obtain an estimate of the long-term exposure patterns that are expected to accompany alternative short-term standard levels. In this regard, the criteria document concluded that significant growth and yield effects could occur if the average ozone concentration exceeds 0.05 ppm (98 $\mu g/m^3$) beyond 15 days.[31] Based on the evidence cited in its support, this conclusion is for the purposes of this document interpreted to mean 15 consecutive days with maximum 8-hour-average concentrations above 0.05 ppm. The analytical criteria indicated by this conclusion provides the basis for evaluating alternative standards levels with respect to their long-term impacts on vegetation.

Unfortunately, this criteria cannot be rigorously evaluated using the computational methods presented in this appendix. These procedures can only predict the number of times a given exposure level will be exceeded in a year, and do not address the probability that such exceedances will occur on consecutive days. This means that using these methods to analyze alternative standard levels with regard to the above criteria inherently introduces a bias towards overestimating their long-term impacts on vegetation.

The existence of this bias indicates the need for caution in interpreting the results obtained by these procedures. Nevertheless, EPA has judged that these methods are the best analytical techniques currently available to evaluate the long-term impacts on vegetation for alternative standard levels, and -- recognizing their limitations -- has used them accordingly. The results are indicated in the table below. For several alternative hourly average standards, the 8-hour frequency distribution was analyzed in the same manner as in the previous section. In this case, the quantity being evaluated was E, the expected number of 8-hour average concentrations per year above 0.05 ppm (98 $\mu g/m^3$). This was obtained from the following modification of the Weibull frequency distribution equation:

$$E = n \exp - \left[\frac{c}{\delta_{8hr}} \right]^{k_{8hr}} \qquad \text{(B-13)}$$

Table B-2

Long-Term Ozone Exposure Patterns Expected to Accompany Alternative Hourly Average Standards

c_{std}, ppm ($\mu g/m^3$)	E, expected number of 8-hour-average concentrations per year above 0.05 ppm (98 $\mu g/m^3$)
0.06 (118)	0
0.08 (157)	2
0.10 (196)	10
0.12 (235)	31

Contravening the aforementioned bias toward overestimating the long-term impacts on vegetation for a given standard level, other uncertainties involved in this analysis tend to underestimate the impacts. For example, the analysis does not examine the possibility that in rural areas the rate of decrease of peak concentrations with increasing averaging times may be lower than in the urban areas for which there are sufficient data to assess such rates of decrease. In other words, it is uncertain what relationships might be valid between the k parameters for different averaging times at representative rural sites. It seems plausible that these relationships would be such that higher 8-hour-average peak concentrations would result at a rural site than at an urban site if both were meeting the same hourly average standard, due to the higher levels of ozone-scavenging anthropogenic pollutants (such as NO) at the urban sites. Nevertheless, it was necessary to use urban relationships to conduct the foregoing analysis because the rural relationships (which are admittedly more pertinent to the issue of a secondary standard) have not been quantified.

Another uncertainty in the air quality estimates is provided by the fact that, for 3- and 8-hour averaging times, the data were evaluated for only the 8 and 3 time periods, respectively, that coincide with a calendar day. If the data were analyzed so as to examine all possible 3- and 8-hour periods (i.e., a "running average" analysis), it seems likely that higher 3- and especially 8-hour-average peaks would be associated with a given hourly average standard. This is because the maximum ozone levels tend to occur in the afternoon hours (approximately 12 p.m. through 8 p.m.), which period is split by examining the three 8-hour periods that coincide with a calendar day (12 a.m. - 8 a.m., 8 a.m. - 4 p.m., and 4 p.m.- 12 a.m.). Unfortunately, the analysis of air quality data that was performed in this appendix was not capable of evaluating "running averages", so this uncertainty must be weighed into the examination of alternative standard levels.

A further uncertainty involved in interpreting Table B-2 with respect to the adequacy of a particular standard level lies in the possible interactive effects of ozone with other pollutants. The conclusion of the criteria document that significant growth and yield effects could occur if the (8-hour) average concentration exceeded 0.05 ppm beyond 15 days was based on studies examining controlled exposures of plants to filtered air to which only ozone had been added. The simultaneous presence of non-ozone oxidants (such as PAN) or other pollutants such as SO_2 in the ambient air could produce synergistic effects if the specified ozone concentration were exceeded for fewer than 15 days.

Because of the uncertainties discussed above, it is concluded that a 0.10 ppm standard level may not in fact be sufficiently stringent to protect against significant growth and yield effects due to the long-term exposure patterns expected to accompany that standard. It does appear that a 0.08 ppm standard level would be adequate for this purpose.